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ADVANCES IN PHYSICS

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Antiferromagnetism

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CONTENTS

§ 1. Introduction.

PART I. FUNDAMENTAL FACTS AND ELEMENTARY THEORY

- § 2. Antiferromagnetic arrangement as revealed by neutron diffraction and other experiments.
- § 3. Susceptibility, specific heat and other properties.
- § 4. Theory of the susceptibility at low field strengths.
- § 5. Theory of the susceptibility at moderately high fields.
- § 6. Antiferromagnetic resonance.
- § 7. Transition from antiferromagnetic to paramagnetic state under a high field.

PART II. INDIRECT EXCHANGE INTERACTION AND ANISOTROPY ENERGY

- § 8. Superexchange and double exchange interactions.
- § 9. Origin of the anisotropy energy.
- § 10. Anisotropy energy in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.
- § 11. Anisotropy energy in MnF_2 , FeF_2 , and CoF_2 .

PART III. STATISTICAL THEORY OF ANTIFERROMAGNETISM

- § 12. General remarks.
- § 13. High-temperature approximations.
- § 14. Low-temperature approximation and the antiferromagnetic ground states.
- § 15. The semi-classical theory of the spin-wave in antiferromagnetic lattices.
- § 16. The quantum-mechanical formulation of the spin-wave theory.
- § 17. Consequences of the spin-wave theory.
- § 18. Further remarks and summary.

§ 1. INTRODUCTION

THE present review article aims at bringing out essential features of the development of the theory of antiferromagnetism together with some of the experimental facts hitherto obtained. In 1950, at the International Conference on Ferromagnetism and Antiferromagnetism at Grenoble, van Vleck gave an excellent review of the theoretical side of the same subject and Bizette of the experimental side and these have been published in *Le Journal de Physique et le Radium* (1951). Since then, however, a considerable advance has been made in this field, notably in the study of the resonance absorption of microwaves, the problem of anisotropy energy, spin-wave theory, structure determination by means of neutron diffraction and of proton resonance absorption, and so on. The present article inevitably overlaps to some extent with those of van Vleck and Bizette, but is concerned more with these recent advances. The same field is also covered, though in less detail, by Lidiard (1954).

The concept of antiferromagnetism was first put forward by Néel (1932 a) in connection with his study of the paramagnetic susceptibility of metals and alloys of transition elements. He noticed that metals such as Pt, Pd, Mn, Cr or alloys such as Pt-rich Pt-Co and Pd-rich Pd-Ni show an almost temperature-independent susceptibility which is too large to be explicable in terms of Pauli's free electron paramagnetism. He supposed that the atoms of these substances possess magnetic moments and that a negative exchange coupling is operating among them. As a consequence, he guessed that the arrangement of the atomic magnetic moments in the crystal lattice is such that they point upward and downward in an alternating manner when the temperature is sufficiently low. He showed through a simple calculation that the susceptibility of such a system is nearly constant at low temperatures and obeys at high temperatures the Curie-Weiss law

$$\chi = \frac{C}{T + \Theta}, \quad (1.1)$$

with a negative paramagnetic Curie temperature $-\Theta$. He also (Néel 1932 b) made measurements with Mn and Cr diluted in noble metals and found that these atoms actually possess a magnetic moment of 4 to 5 μ_B (μ_B is a Bohr magneton) and suggested for pure Mn and Cr values of Θ higher than 1000°K.

Néel (1936 a and b) extended his experiments to other systems of alloys and worked out his theory more in detail. In these works the following points may be noticed: (1) He studied the magnetic properties of binary alloys of two transition elements, using the Weiss molecular field approximation. This problem was studied by himself in greater detail in connection with ferrites (Néel 1948). (2) A formula for the antiferromagnetic Curie point was derived with the same approximation. (3) By plotting the coefficient of the Weiss field deduced from experiment against $d - \delta$, namely the difference between the atomic distance d in the

metals, or the alloys, and the mean diameter of the d-shells of the constituent atoms δ , he found that the points fall on a smooth curve whose positive part corresponded to ferromagnets and the negative part to antiferromagnets. (4) The anisotropy energy in antiferromagnetic substances was suggested to be of the same order of magnitude as in ferromagnetic ones, and the susceptibility at absolute zero was computed for the case of uniaxial anisotropy as a function of the intensity and direction of the applied magnetic field. An interesting result of this analysis is the existence of a certain critical field strength, H_c , for the case where the field is applied along the axis of easy magnetization. The antiparallel magnetizations of the two sublattices turn from the direction of the easy axis to that perpendicular to it when the field exceeds this critical value. This topic will be dealt with in detail in § 5 of the present article, but a preliminary representation of it might conveniently be given here as follows:—

Suppose we have an anisotropy energy (per unit volume) of the form $K \sin^2 \phi$, where K is a positive constant and ϕ the angle between the easy axis and the direction of the magnetization. We shall use the notation Δ for the latter. If the external field is parallel to this direction Δ , the induced magnetic moment of the system will also be parallel to it. We shall denote the corresponding susceptibility as χ_{\parallel} . If the magnetic field is perpendicular, the induced moment will likewise be perpendicular; the corresponding susceptibility will be denoted as χ_{\perp} . It can be shown that χ_{\perp} is independent of temperature to a good approximation, that χ_{\parallel} decreases with decreasing temperature, vanishing at absolute zero, and that $\chi_{\parallel} = \chi_{\perp}$ at the antiferromagnetic Curie temperature. Now suppose an external magnetic field H is applied along the easy axis. Initially the direction Δ coincides with this axis, and the change in free energy per unit volume of the system is given by $-\chi_{\parallel} H^2/2$. With increasing field strength, however, this change in free energy becomes equal to $K - \chi_{\perp} H^2/2$, that is, the free energy for Δ perpendicular to the easy axis, and then exceeds it, since in general $\chi_{\perp} > \chi_{\parallel}$. The critical field is obtained by solving the equation

$$-\frac{1}{2}\chi_{\parallel}H^2 = K - \frac{1}{2}\chi_{\perp}H^2$$

or

$$H_c = \{2K/(\chi_{\perp} - \chi_{\parallel})\}^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad (1.2)$$

This remarkable phenomenon of the ‘flopping’ of the direction Δ was actually observed by Gorter and his co-workers (1951-53) in single crystals of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. This substance has a *Néel point*—another name for the antiferromagnetic Curie point initiated by these authors—of 4.3°K and is orthorhombic. In the orthorhombic case, the magnetization vectors turn from the direction of the easy axis to that of the intermediate axis. Up to the present, however, in no other substance has this phenomenon been observed, presumably because in most substances the value of the critical field strength is too high.

In the early days Néel employed the expression *paramagnétisme constant* for *antiferromagnetism*. The latter term can be traced back to Hulthén's work (1936, 1938) in which the first spin-wave treatment of antiferromagnetism was given. (Prior to that, an approximate quantum-mechanical solution of antiferromagnetism for the case of one dimension had been given by Slater (1930) and the exact solution of it by Bethe (1931); the latter treats one-dimensional ferromagnetism, but the sign of the exchange integral can be reversed without modifying the formalism.) Considerable advances have since been made in the spin-wave theory by Anderson (1951, 1952), Ziman (1952-53), Kubo (1952, 1953), Nakamura (1952), Tessman (1952), Keffer, Kaplan and Yafet (1953) and Kasteleijn (1952). On the other hand, Néel's original theory, based on the Weiss approximation, has been extended by Bitter (1937), van Vleck (1941), Néel himself (1948), Anderson (1950 b), Garrett (1951), Nagamiya (1951-54), Yosida (1951-53), Kittel (1951), Keffer and Kittel (1952), Gorter and Haantjes (1952), Ubbink (1953 a, b), Smart (1953), Wangsness (1952-53), and possibly by others. Among these authors, Néel and Anderson, as well as Smart, recognized the importance of the next-to-nearest neighbours for the Néel point and the susceptibility, Kittel, Nagamiya, Yosida, Keffer and Kittel, Gorter and Haantjes, Ubbink and Wangsness treated the problems connected with the anisotropy energy and the resonance absorption of microwaves by antiferromagnetic substances, and Bitter, Garrett and Leiden workers under Gorter considered, among others, the case in which the applied magnetic field is of the order of, or greater than, the Weiss molecular field. At present, only a few substances are known in which the last mentioned case is really important.

A number of papers also appeared which tried to improve the statistical-mechanical treatment of the problem. Li (1951) applied the Bethe-Peierls-Weiss method to antiferromagnetism, Nakamura (1953) applied another similar method, and Kubo and his co-workers (1951-52) and also Oguchi and Obata (1952) developed a moment expansion method and other expansion methods in antiferromagnetism.

The resonance absorption of a microwave by antiferromagnets was first attacked experimentally by Trounson, Bleil, Wangsness and Maxwell (1950) with a polycrystal of Cr_2O_3 . They observed no remarkable effect below the Néel point, because the resonance frequency in this substance should lie in the sub-millimeter region according to theory. Ubbink (1951-53) at Leiden, however, discovered peculiar resonance phenomena in the single crystal of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which have been explained by his own theory and that of Nagamiya and Yosida.

A fundamental problem of antiferromagnetism is the origin of the exchange interaction. Bizette (1946) and Néel (1948) recognized for antiferromagnetic compounds the importance of superexchange, that is, the exchange coupling between magnetic atoms through the intermediary of a negative non-magnetic ion. This sort of interaction was first considered by Kramers (1934) and its realistic treatment was given by

Anderson (1950 a). For metallic antiferromagnets a band-theoretical treatment might be useful, and attempts of this kind have been made by Matsubara (1953) and Lidiard (1953) following a suggestion made by Slater (1951), who with Pratt (1953), also considered another mechanism of superexchange for compounds.

Another fundamental problem of antiferromagnetism is the origin of the anisotropy energy, which was studied by Keffer (1952), Yosida (1952), Moriya and Yosida (1953), Niira and Oguchi (1954) and Nakamura and Taketa (1954) for a few substances.

So far we have cited mainly theoretical works, but there are great many valuable experimental studies. It is not convenient to cite them in this introduction, but we shall summarize them in the next two sections and refer to them where appropriate elsewhere.

PART I. FUNDAMENTAL FACTS AND ELEMENTARY THEORY

§ 2. ANTIFERROMAGNETIC ARRANGEMENT AS REVEALED BY
NEUTRON DIFFRACTION AND OTHER EXPERIMENTS

It may be useful first to present some experimental results on the magnetic structure of a number of antiferromagnetic substances.

The most direct method of determining the arrangement of spins in an antiferromagnetic crystal is that of neutron diffraction. An ordinary Debye-Scherrer pattern is obtained by passing a monochromatized neutron beam through a powdered sample, the neutrons being scattered by the nuclei and by the magnetic moments of the atoms. From the latter the direction of the magnetization can be definitely determined in most cases, but the superstructure arrangement of positive and negative spins seems to be less definitely determined since one has to depend on the method of trial and error. X-ray analysis also gives an indication of the superstructure, though indirectly. In the case of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, proton magnetic resonance was useful for the superstructure determination.

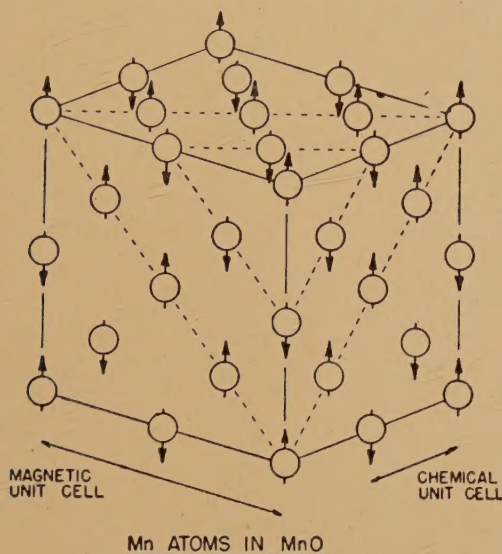
MnO , FeO , CoO , NiO , MnS , MnSe are all of the NaCl-type. Shull and his co-workers (1949, 1951 b) found for them by neutron diffraction that the magnetic atoms on each (111) plane have the same direction of spins and that the direction alternates as one goes from one (111) plane to the adjacent one. In MnO , MnS , MnSe , CoO and NiO , the direction of spins was found to be one of the cubic principal axes, so that the symmetry of the spin arrangement is monoclinic. In FeO , however, the spin direction was found to be [111], the symmetry thus being rhombohedral. X-ray analysis of these compounds, except MnSe , has been carried out by Rooksby (1943, 1948), Tombs and Rooksby (1950, 1951), Shimomura and Nishiyama (1948, 1949), Shimomura (1953), Greenwald and Smart (1950, 1951) and Greenwald (1953). They found that all these substances, except CoO , deform slightly below the Néel point and become rhombohedral, a change (contraction except in FeO) of a fraction of 1% occurring along the [111] direction. The atoms with opposite spins thus appear to attract each other in most substances, while magnetostriction appears to be of minor importance. In CoO , the lattice deforms tetragonally, a contraction occurring along one of the original cubic axes. There is at present no reasonable explanation for this if one assumes the evidence of neutron diffraction to be conclusive. Shimomura (1953) dissolved copper oxide in NiO and observed the change in lattice constant as a function of the copper concentration; above 21.5 atomic per cent Cu, the lattice was found to be perfectly cubic, but at 24% he still found antiferromagnetism. It may, however, be premature to conclude that in the

latter case the exchange force is inactive in deforming the lattice, since we do not know the magnetic structure of this solid solution.

Greenwald (1953) observed also in hexagonal antiferromagnetic compounds, Cr_2O_3 and MnTe , a contraction along the principal axis, which increased as the temperature was lowered from the Néel point.

MnO_2 is another antiferromagnetic substance. It is tetragonal body-centred, and the suggested magnetic structure on the basis of neutron diffraction (Erickson 1952) is such that the corner atoms and the body-centred atoms form separate antiferromagnetic superstructures, the directions of the magnetizations of the two being normal to the c -axis and at right angles to each other, possibly one pointing in $[110]$ and the other in $[1\bar{1}0]$.

Fig. 1



Antiferromagnetic structure existing in MnO below its Néel temperature of 120°K . The magnetic unit cell has twice the linear dimensions of the chemical unit cell. Only Mn ions are shown in the diagram. (After Shull, Strauser and Wollan 1951 b.)

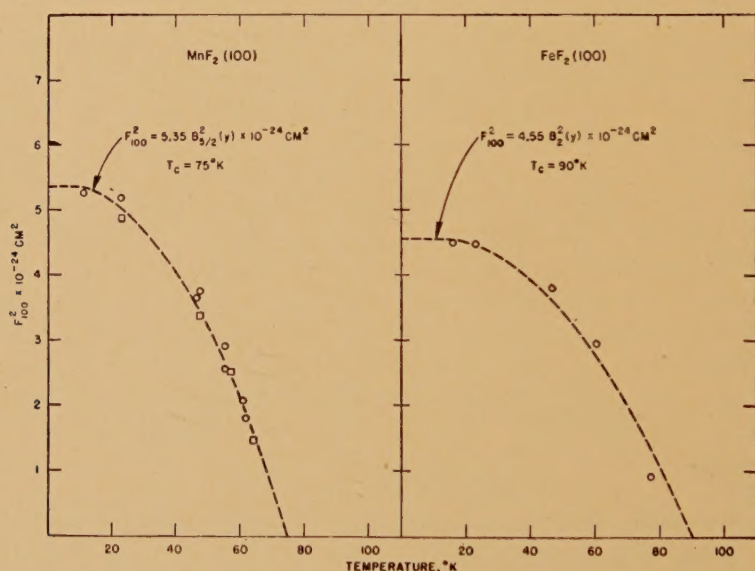
The magnetic structure of CrSb (NiAs-type) was investigated by Snow (1952) and the spins were found to point parallel to the c -axis, the atoms in the same (001) plane pointing in the same direction and the atoms in the adjacent (001) plane in the opposite one.

MnF_2 , FeF_2 , CoF_2 and NiF_2 are all of the rutile type. Except in NiF_2 , the metallic atoms at the corners of the tetragonal unit cell point downwards and those at the body-centres point upwards (Erickson and Shull 1951, Erickson 1953). In NiF_2 the spin direction does not appear to coincide exactly with the c -axis but is inclined to it at an angle of 10° , possibly pointing to one of the neighbouring fluorine ions. Erickson

determined the magnitude of the spontaneous magnetization of each sublattice as a function of temperature from the observed intensity of the 100 line. It was well represented by the Brillouin function (see § 4), with $S=5/2$, 2, $3/2$ and 1, respectively, for the fluorides of Mn, Fe, Co and Ni. Figures 2 and 3 show his results. At the same time he found the Landé factors to be 1.99, 2.32, 2.00 (2.03 from the diffuse scattering above the Néel point) and 2.04, respectively.

The oxide, α -hematite, Fe_2O_3 , is interesting in that it shows a feeble ferromagnetism, possibly due to the presence in it of parasitic ferromagnetic substances. The main structure is without doubt antiferromagnetic, and its structure was determined by Shull, Strauser and Wollan (1951 b) as shown in fig. 4. The figure also shows the structure found in Cr_2O_3 (Brockhouse 1953). Below -20°C , the direction of the spins is parallel to the crystallographic principal axis, but perpendicular above.

Fig. 2

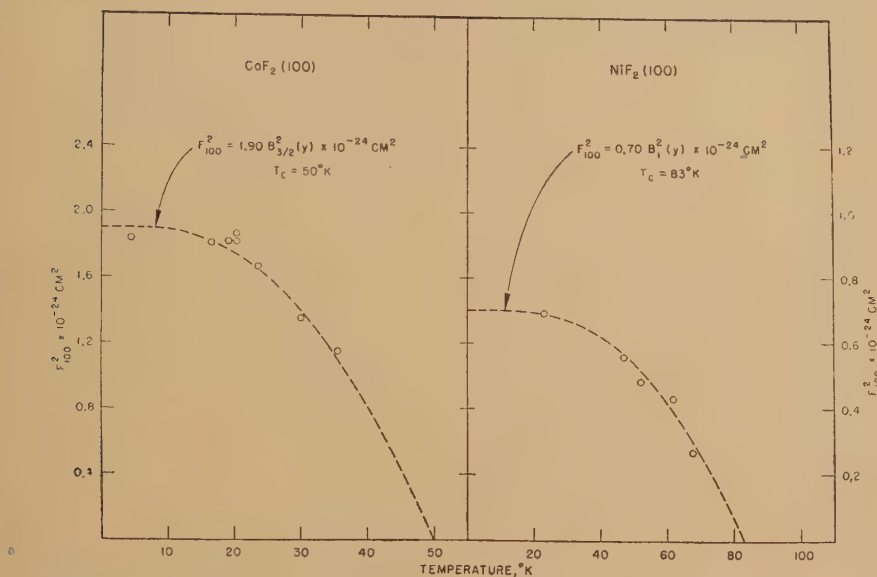


Temperature dependence of the 100 peak intensity of the diffracted neutron beam, in terms of the crystal structure factor, for MnF_2 and FeF_2 . The points are fitted with an appropriate Brillouin saturation curve. (After Erickson 1953.) T_c stands for our T_N .

At this temperature an anomaly of the susceptibility has been observed, and will be referred to later (§ 3). The neutron diffraction measurements were done between 80°K and 1000°K , that is, up to a temperature a little over the Néel point. It was found that the intensities of the diffraction lines, which should be proportional to the square of the spontaneous magnetization, decrease linearly with temperature over a wide range from 250°K to 1000°K . More detailed measurements in the neighbourhood of -20°C have been made by Corliss, Hastings and Goldman (1954).

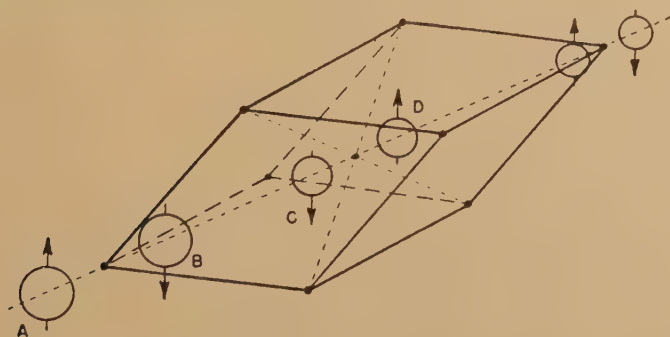
Some of the ferrites, such as ZnOFe_2O_3 , seem to be antiferromagnetic. The neutron diffraction experiment reveals not only whether the ferrite is normal or inverse but also the direction of the spontaneous magnetization of the sublattices. In all cases hitherto investigated (ferrites of Fe,

Fig. 3



Temperature dependence of the (100) crystal structure factors in CoF_2 and NiF_2 . The saturation curves indicate Néel temperature of 50°K for CoF_2 and 83°K for NiF_2 . (After Erickson 1953.) T_c stands for our T_N .

Fig. 4



Magnetic structure of $\alpha\text{-Fe}_2\text{O}_3$ at room temperature. The rhombohedral unit cell containing four unique iron atoms is shown. (After Shull, Strauser and Wollan 1951 b.)

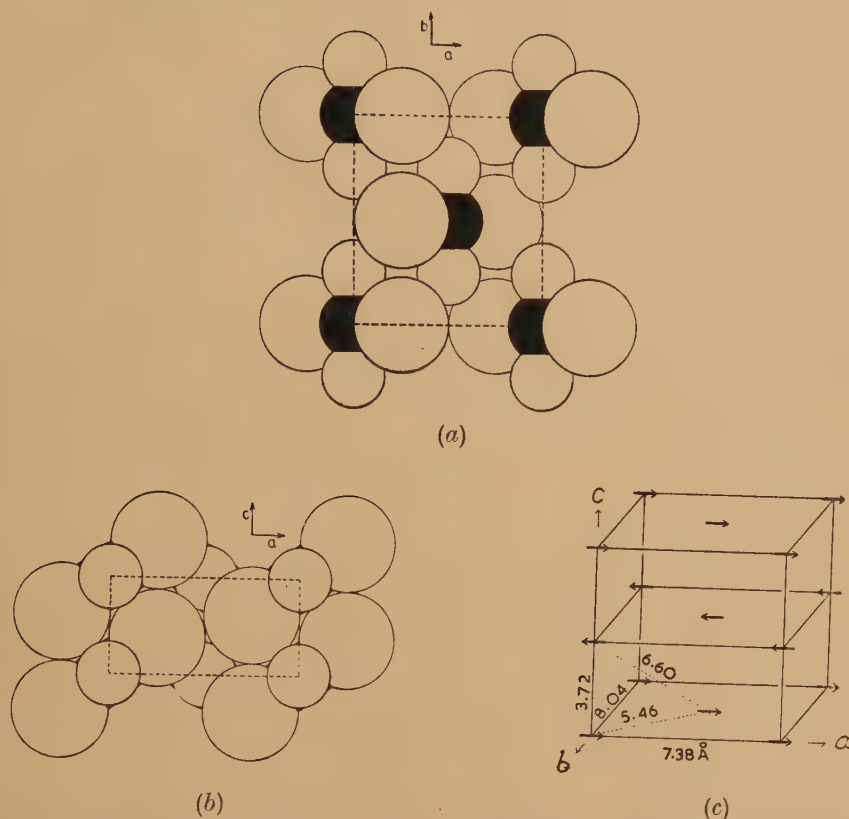
Ni, Mg and Zn), except in ZnOFe_2O_3 , the spins on one of the two sublattices were found to point in the opposite directions to those on the other sublattice, as predicted by Néel (1948), and the preferred direction

to be one of the cubic axes (Shull, Wollan and Strauser 1951 a, Hastings and Corliss 1953, Corliss, Hastings and Brockman 1953). In ZnOFe_2O_3 no coherent magnetic scattering was observed at room temperature, possibly because the Néel temperature is at liquid air temperatures.

A number of transition metals have also been investigated by Shull and Wilkinson (1953). In V, Nb, Mo and W, no measureable magnetic scattering lines, neither diffuse nor sharp lines, were observed. In Cr and α -manganese, however, an antiferromagnetic arrangement was observed, which varied as a Brillouin function, and the suggested Néel points are 473°K and 100°K respectively. The atomic magnetic moment deduced from the intensity of lines for aligned moments in Cr and that deduced from the diffuse lines above the Néel point in Mn are $0.40\mu_B$ and about $0.5\mu_B$ respectively, not 4 and $5\mu_B$ as one would expect. Néel (1932 b) obtained the latter values from magnetic measurements on these metals dissolved in noble metals. A test was done for Cr at another neutron velocity 25% higher, as there was a suspicion that a rapidly changing polarity of the moment might have affected the observed value of the moment. No effect was found, however. Néel (1953 b) points out a possibility that the observed moment is concerned with the moment of those Cr atoms which are situated in the regions where impurity atoms stabilize the antiferromagnetic sublattices in such a way as to fix their polarities during the passage time of neutrons. A band-theoretical treatment of antiferromagnetism, or a collective electron antiferromagnetism, worked out by Matsubara (1953) and also by Lidiard (1953) predicts a small effective moment and thus agrees with experiment, but Anderson (1953) remarks that a theory of this type is inappropriate in the case where a form-factor scattering is observed above the Néel point, as in the case of Mn. His criticism may be valid if the theory is understood in its naive sense. The low values of the Néel point are also contradictory to those suggested by Néel from magnetic measurements. We shall return to these topics in the next section.

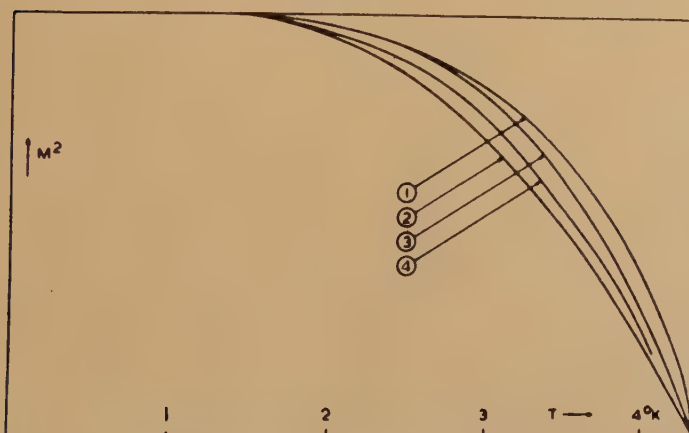
So far we have summarized the results obtained by neutron and x-ray diffraction experiments. There is a proton resonance experiment in the case of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Poulis and Hardeman 1952 a, b). This substance has a Néel point of 4.3°K and is most interesting from various points of view, as we shall see in later sections. The ordered arrangement of the cupric ions will produce different internal magnetic fields at different proton positions and thus will cause a splitting of the proton resonance line. The magnetic unit cell obtained by Poulis is shown in fig. 5 (a) which is twice as large as the chemical unit cell along the c -axis (fig. 5 (a) and (b)). The spins point parallel to the a -axis if there is no external field, but they turn to the b -axis when a field greater than H_c , the critical field strength, is applied along the a -axis. Figure 6 shows the magnetization as a function of temperature, deduced from proton and microwave resonance experiments, from specific heat measurement, and that calculated on the basis of Weiss molecular field approximation.

Fig. 5



The crystal structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. (a) Projection on (001), (b) Projection on (010). Large open circles represent Cl atoms, small open circles O atoms and black circles Cu atoms. (After Harker 1936.)

Fig. 6



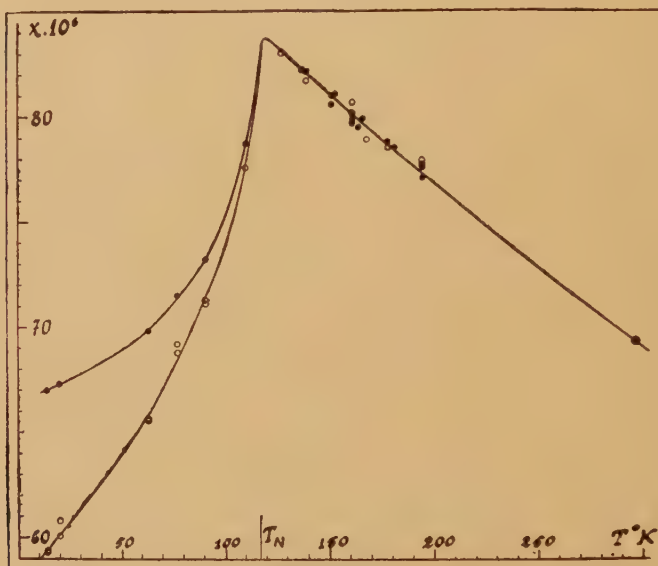
The square of the magnetization per sublattice as a function of temperature for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Curve 1: from the proton resonance measurements of Poulis, curve 2: from the molecular field theory with $S=1/2$, curve 3: from the specific heat measurements of Friedberg, curve 4: from H_c and α ; see § 6. (After Ubbink 1953 a.)

§ 3. SUSCEPTIBILITY, SPECIFIC HEAT AND OTHER PROPERTIES

Of the many experiments on susceptibility and other properties only a few typical ones will be quoted here.

The earliest measurements of the susceptibilities characteristic of anti-ferromagnetic materials are, as far as the writers could find, those done in Japan by Honda and his co-workers (Honda and Soné 1914, Ishiwara 1914, Honda and Ishiwara 1915), together with Weiss and Foëx's (1911) measurements of the susceptibility of γ -Fe which exists in a limited range of temperature with no Néel point in that range. They investigated MnO, Cr_2O_3 , CuBr_2 , CuO and NiO between liquid air temperature and 1000°C ,

Fig. 7



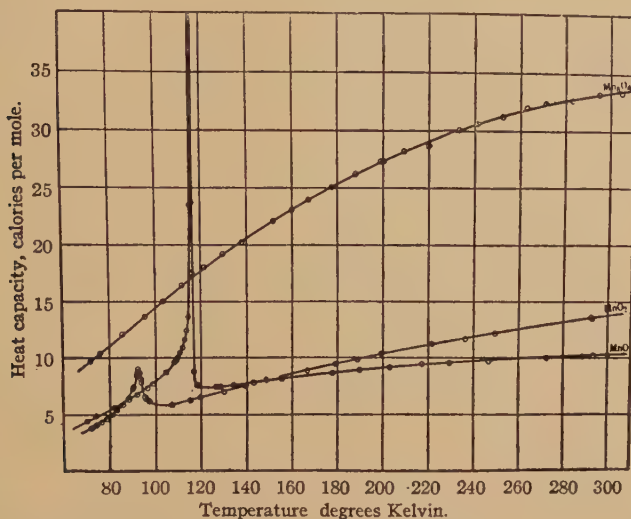
Magnetic susceptibility of MnO. White circles are for $H=5000$ oe and black circles are for $H=24000$ oe. (After Bizette, Squire and Tsai 1938.)

and later (Shimizu 1930) Mn between room temperature and 1250°C . A well-defined peak in the susceptibility-temperature curve was found in MnO at 108°K , a fairly well-defined peak in Cr_2O_3 in the neighbourhood of 40°C and a broad peak in other substances. Bizette, Squire and Tsai (1938) extended the range of temperature to 14°K and worked possibly with a better sample of MnO, because they obtained lower susceptibility values. The Néel point was found to be 116°K and the susceptibility above the Néel point was found to obey the Curie Weiss law (1.1), with $\Theta=610^\circ\text{K}$ and $C=4.40$ deg. cm^3 mole, or an effective atomic moment of $5.95\mu_B$ (theoretically, $5.92\mu_B$ for spin 5/2). Figure 7 shows their result. Similar results were obtained for Cr_2O_3 by Foëx and Graff (1939), Foëx and Wucher (1951) and McGuire (quoted in the paper of Trounson *et al.*

(1950)). There are many other substances which show similar properties ; we summarize the data in table 1.

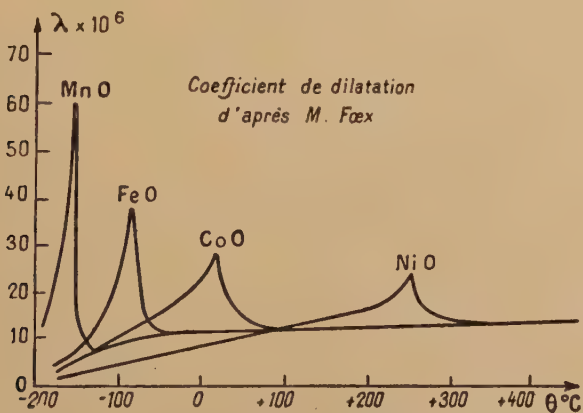
Antiferromagnetic substances usually show a λ -type anomaly at the Néel point in their specific heat curves. Figure 8 shows an example obtained by Millar (1928) for manganese oxides. The thermal expansion

Fig. 8



The molal heat capacities of MnO, Mn₃O₄ and MnO₂. (After Millar 1928.)

Fig. 9



Thermal expansion coefficients of MnO, FeO, CoO and NiO. (After Foëx 1948.)

coefficient behaves in a similar way ; fig. 9 is due to Foëx (1948). Street and Lewis (1951) and Fine (1953) observed a sudden increase in Young's modulus above the Néel point for NiO and CoO, the temperature coefficient varying somewhat like that of the thermal expansion,

Table 1

Substance	(1)		(2)	(3)
	crystal type	Lattice constant $a, b, c ; \alpha$	Néel temp. T_N °K	
			χ	sp. heat
1 MnO	NaCl*	4.4345 str. trans. to trig. for $< -100^\circ\text{C}$	122	116 ^a 117.8 ^b
2 FeO	NaCl*	4.332 str. trans. to trig. $\alpha < 60^\circ$ for $< -70^\circ\text{C}$	198 ^a 186 ^b	183 ^a 188.5 ^b
3 CoO	NaCl*	4.2495 (20°C) tetr. 4.2552, 4.2058 (-180°C)	293	289.7
4 NiO	NaCl*	4.1684 trig. 4.16768 ; 90° 3.8' (9°C)	492 ~ 647	520
5 CuO	monocl.*	4.653, 3.410, 5.108 ; 99° 29'	~ 453	~ 220 ?
6 V ₂ O ₃	Cr ₂ O ₃	5.43 ; 53° 53'	173	168.8
7 V ₂ O ₄	rutile	4.54, 2.88 $u = ?$	343 ^a 335 ~ 355 ^b	
8 Cr ₂ O ₃	trig.	5.38 ; 54° 50' str. trans. at 307 ~ 318°K	311 ^a 323 ^{b, c} 350 ^d	305 ^a 304.5 ~ 306.5 ^b
9 MnO ₂	rutile*	4.44, 2.89 $u = ?$	84	92.12
10 α -Fe ₂ O ₃	Cr ₂ O ₃ *	5.4135 ; 55° 17'	~ 950	~ 950
11 CrS	NiAs	3.448, 5.754		
12 MnS	NaCl*	5.212	165 ^a	140
13 FeS	NiAs	str. trans. to trig. for $< T_N$ 3.453, 5.670	147 ^b 613	
14 MnSe	NaCl*	5.448		247
15 MnTe	NiAs	4.124, 6.698 sharp contraction of c below 329°K	323 ^{a, c} 307 ^b	307
16 FeTe	NiAs	3.800, 5.651		
17 MnF ₂	rutile*	4.8734, 3.3103 $u = 0.310$	72 ^a 70 ^b	66.5
18 FeF ₂	rutile*	4.670, 3.297 $u = 0.31$	79	78.3
19 CoF ₂	rutile*	4.69, 3.19 $u = 0.31$		37.7
20 NiF ₂	rutile*	4.6505, 3.0837 $u = 0.31$		73.2
21 VCl ₂				
22 VCl ₃			30	104.9?
23 CrCl ₂			40	
24 FeCl ₂	CdCl ₂	6.20 ; 33° 36' $u = ?$	24	23.50
25 FeCl ₃	trig.	6.69 ; 52° 30'		
26 CoCl ₂	CdCl ₂	6.16 ; 33° 26' $u = 0.25$	25	24.90

(4) from other meas.	(5)		(6) ratio of $\chi_{T=0}$ to $\chi_{T=T_N}$	References and remarks (The numbers in brackets refer to the columns, and the numbers which follow refer to the corresponding references.)
	θ	C_{mol}		
116 D	610	4.40	0.69	(1) 97 (2, 5, 6) 11 (3) ^a 66 ^b 96 (4) 34 s.s. CoO 7, FeO 17, MgO 16, 17
186 D	570 ^a	6.24 ^a	0.78 ^a	(1) 97, (2, 5, 6) ^a 15 ^b , ^c 63 (3) ^a 67 ^b 96 (4) 34
	190 ^b	4.60 ^b	0.76 ^b	(5) ^b 196 < T < 460°K ^c 973 < T < 1320°K s.s. MnO 17, MgO 16, 17
	195 ^c	2.42 ^c		
292 D	280	3.0546		(1) 97, 38' (2, 5) 61 (3) 108 (4) 34, 95, 71 s.s. MnO 7, MgO 17, NiO, CuO 108
289 E				
291 S				
523 D			0.67	(1) 86 (2, 6) 61 (3) 112 (4) 34, 95
507 E				
~230 N			0.60	(2, 6) 53 see also 60, (3) 57 (4) 110
170 D				(2) 54 (3) 3 (4) 33
168 C				$\chi = \text{const.}$ in 383 < T < 523°K 31
	720	0.55		(2) ^a 54 ^b 74 (5) 74
305.8 D	1070 ^a	2.56 ^a	0.76 ^a	(1) 38 (2, 5, 6) ^a 100 ^b 30 ^c 52 ^d 32 (3) ^a 4 ^b 56 (4) 56, 71
318 S	550 ^b	1.82 ^b	0.85 ^b	res. 100, 64
	493 ^d			
			0.93	(2, 6) 18 (3) 59 s.c. χ 18
~950 C	2000	4.4		(2, 3, 4) 26 (5) 69 res. 5 anis. change at -10 ~ -30°c accomp. by weak ferro. 23, 70, 19
				CrS _{1+x} $x > 0.14$ shows ferro. 46, 48, 106
	528 ^a	4.30 ^a	0.82 ^a	(1) 79 (2, 5, 6) ^a 17 ^b 88 ^c 81, (3) 2 (6) ^a at $H = 32\,000\phi$
	454 ^c	3.485 ^c	0.76 ^b	res. 64
	857	3.44		(2, 5) 20 trans. at 120°c
				FeS _{1+x} $x > 0.1$ shows ferro. 47, 73, 10, 106
	361	4.01		(3) 58 (5) 81 large therm. hysteresis 13, 62 C 102
	690 ^a	4.59	0.68 ^a > 0.5 ^b	(1) 38' (2, 5, 6) ^a 81 ^b 88 ^c 104 (3) 58 C 89, 102 (5) 103
75 N	220	0.92		
	113.2 ^a	4.08 ^a	0.72 ^a	(1) 39 (2, 5, 6) ^a 12 ^b 25 ^c 22 (3) 91 (4) 27
	97.0 ^c	4.47 ^c	0.78 ^b	s.s. ZnF ₂ 22 $\chi_{\parallel} - \chi_{\perp}$ 92, 40 s.c. χ 109
90 N	117	3.88	0.72	(2, 5, 6) 14 (3) 94 (4) 27 $\chi_{\parallel} - \chi_{\perp}$ 93
50 N	52.7	3.29		(3) 94 (4) 27 (5) 17 see also 24 $\chi_{\parallel} - \chi_{\perp}$ 93
83 N	115.6 ^a	1.528 ^a		(1) 45 (3) 94 (4) 27 (5) ^a 17 ^b 25
	100 ^b	1.3 ^b		weak ferro. appears below T _n 111
	565	2.13		(5) 90
	30.1	1.005	0.72	(2, 5, 6) 90 (3) 84
	149	3.26	0.84	(2, 5, 6) 90
	-48.0	3.59	< 0.2	(2, 5, 6) 90 (3) 98
	11.5	4.07		(5) 90
	-38.1	3.46	~0.6	(2, 5, 6) 90 (3) 99

Table 1—cont.

Substance	(1)		(2)	(3)
	crystal type	Lattice constant $a, b, c; \alpha$	Néel temp. T_N °K	
			χ	sp. heat
27 NiCl ₂	CdCl ₂	6.13 ; 33° 36' $u=?$	50	52.35
28 CuCl ₂			70	
29 CuBr ₂			193	
30 CrSb	NiAs	4.107, 5.468	~673	
31 MnAs	NiAs	3.710, 5.691 (<45°C) 3.659, 5.691 (>45°C)	399	~45 lat. heat
32 MnBi	NiAs	4.30, 6.12 $c=6.11 \rightarrow 5.82$ at 350°C		621 ~633 718 (lat. heat)
33 Cr	b.c.c.	2.8796	~1673	
34 α -Mn	complex			95
35 MnCl ₂ · 4H ₂ O			~1.68	1.622
36 MnBr ₂ · 4H ₂ O			~2.2	
37 CuCl ₂ · 2H ₂ O	rhomb.*	7.38, 8.04, 3.72		4.31
38 Co(NH ₄) ₂ · (SO ₄) ₂ · 6H ₂ O	monocl.	9.23, 12.49, 6.23 ; 106° 56'		0.084
39 FeCO ₃	NaNO ₃	5.754 ; 47° 25' $u=0.27$		
40 FeCO ₃ · 2MgCO ₃				

Those marked with * in column 'crystal type' have known spin super structures ; for the detail see text §2.

† Phase diagram in H - T -plane for antiferromagnetism \rightleftharpoons paramagnetism (or \rightleftharpoons ferromagnetism) is measured.

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(4) from	(5)		(6) ratio of $\chi_{T=0}$ to $\chi_{T=T_N}$	References and remarks (The numbers in brackets refer to the columns and the numbers which follow refer to the corresponding references.)
	θ	C_{mol}		
other meas.				
723 D	-68.2	1.36	0.64	(2, 5, 6) 90 (3) 21
	109	0.536		(2, 5, 6) 90
	~1000			(2) 53 see also 60
	-293	2.60		(2, 5, 6) 30 (4) 87
475 N			~ $\frac{1}{4}$	(1, 2, 3, 5) 42 res. 1 ferro. disapp. ~40°C 42
				Mn ₂ As shows antiferro. 43, 44
				(1, 3) 42. res. 1 ferro. disapp. 340 ~360°C 42
320 E?				(2) 65 see also 8 (4) 85 ; 29, 78 C etc. 29 sp.
				heat 6, 28, 107
				s.s. Au 68
				(3) 83 (4) 85 χ 82, 41, 80 C, TEP 72
100 N				s.s. Cu, Ag 68
				(2) 50 51(3) 36 (†) 51
				(2) 51 (†) 51
4.337 PR	5	$C_a=0.447$		(1) 49, 75, 55 (3) 35 (4) 75 (5) 105
		$C_b=0.386$		s.c. res. 101 s.c. PR 75, 76, 77
				(3, 5) 37 (†) 37
K_1 0	0.005 ; K_2 0.017 [§]			
35 Op	K_3 -0.050			
	14	3.49		(4, 5) 17 $\chi_{\parallel}-\chi_{\perp}$ 17
				Op 9, 17

§ Paramagnetic Curie temperatures along three magnetic principal axes, K_1 , K_2 in ac -plane and K_3 parallel to b -axis.

Abbreviations : D, dilatometric measurements ; E, elastic constants anomaly ; S, solubility in H_2SO_4 ; C, conductivity ; N, neutron diffraction ; PR, proton resonance ; s.s., solid solution with ; s.c., single crystal measurements ; TEP, thermoelectric power ; Op, optical measurements.

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Halides of the iron group are also typical antiferromagnetics. They show similar properties to the oxides cited above. We will cite three experimental facts :

1. As in the case of MnO (fig. 7), the susceptibility of MnF_2 has been found to depend on the measuring field strength below the Néel point of 72°K (Bizette and Tsai 1939, de Haas, Schulz and Koolhaas 1940). Theory predicts (see § 5) a dependence on H^2 of the susceptibility, but the measurements are not accurate enough to decide whether it changes proportionally to H or H^2 .

2. Stout and Griffel (1949), Griffel and Stout (1950) and Stout and Matarrese (1953) observed the parallel and perpendicular susceptibilities of MnF_2 , FeF_2 and CoF_2 in single crystals. The results are as seen in figs. 10–12. The susceptibility χ_{\parallel} , with spins and field parallel to the tetragonal axis, goes down to zero as the temperature decreases to absolute zero and the susceptibility χ_{\perp} , with spins parallel but field perpendicular to the tetragonal axis, is nearly constant, though it varies slowly with temperature. Experiments give their difference, and the separate values were obtained by combining it with the susceptibility of the powdered specimens. There is a pronounced anomaly below and above the Néel point. Yosida (1951) gave a rough theoretical estimate of the anisotropy, $\chi_{\perp} - \chi_{\parallel}$, above the Néel point for MnF_2 and Niira and Oguchi (1954) analysed the data for FeF_2 to a certain extent (see § 11). Evidently, we have here (except in MnF_2) to do with the splitting of the electronic energy levels of the magnetic ions in the crystalline electric field, and for the complete understanding of the susceptibility curves it would be necessary to do an elaborate statistical-mechanical treatment.

3. The specific heat of MnF_2 measured by Stout and Adams (1942) shows a sharp peak at the Néel point as in the case of manganese oxides (fig. 13). The change of entropy corresponding to excess specific heat over its normal values has been estimated to be 1.2 cal/deg. mole, which is close to $R \ln 2 = 1.377$. This fact shows that here we are really concerned with an order-disorder phase change between two orientations of the spins. In other cases, such as VCl_2 , the values of the excess entropy reported are smaller.

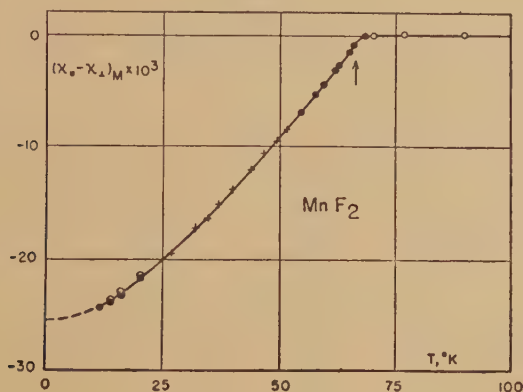
Recent susceptibility measurements by Bizette and Tsai (1954) with a single crystal and a powder specimen of MnF_2 give the following interesting results. The molal perpendicular and parallel susceptibilities and powder susceptibility between liquid helium temperature and room temperature are :

T ($^\circ\text{K}$)	4	14	20	35	63	77	90	195	293
$10^3 \chi_{M\perp}$	24.4	24.4	24.4	24.2	24.1	23.5	22	14.5	10.8
$10^3 \chi_{M\parallel}$	—	1	3.2	21.5	—	—	—	—	—
$10^3 \chi_{Mp}$	16.3	16.6	17.3	23.3	—	—	—	—	—

$\chi_{\perp} - \chi_{\parallel}$ was found to agree with the results of Stout and Griffel, while χ_{\perp} and χ_{\parallel} differ considerably from those given by these authors ; in

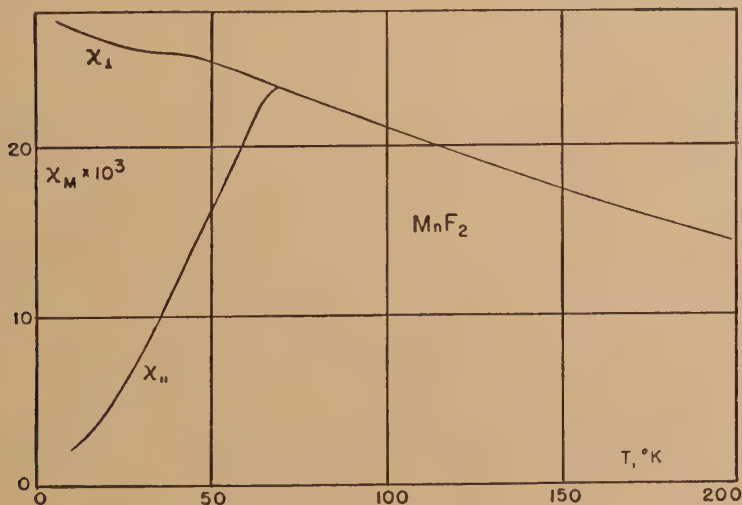
particular, χ_{\perp} remains nearly constant below $T_N=70^{\circ}\text{K}$. The powder specimen was such that the powders were fixed in paraffin, and it was found that the susceptibility did not depend on applied field between 5000

Fig. 10



(a)

The molal magnetic anisotropy of MnF_2 . χ_{\parallel} and χ_{\perp} are molal susceptibilities parallel and perpendicular to the c -axis. The arrow indicates the temperature of the heat capacity maximum. (After Griffel and Stout 1950.)



(b)

Molal magnetic susceptibilities of MnF_2 parallel and perpendicular to the c -axis of the crystal. (After Griffel and Stout 1950.)

and 23 000 oe, contrary to the previous measurements. This is surprising and its theoretical interpretation is hardly possible at present.

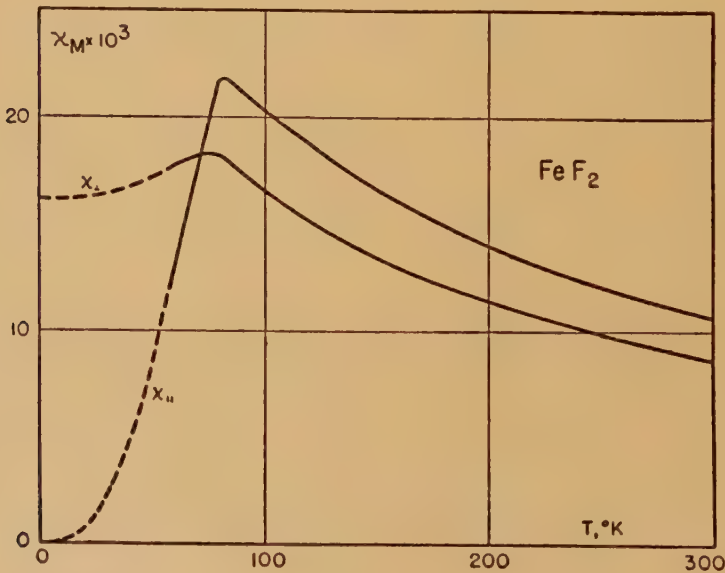
Matarrese and Stout (1954) observed in NiF_2 a weak ferromagnetism below its Néel temperature of 73.2°K . They measured the torque on a

Fig. 11



(a)

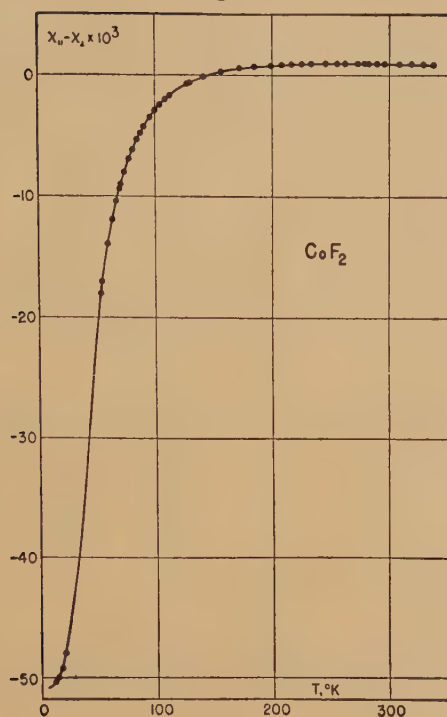
Molal magnetic anisotropy of FeF_2 . $\chi_{||}$ and χ_{\perp} are molal susceptibilities parallel and perpendicular to the c -axis. (After Stout and Matarrese 1953.)



(b)

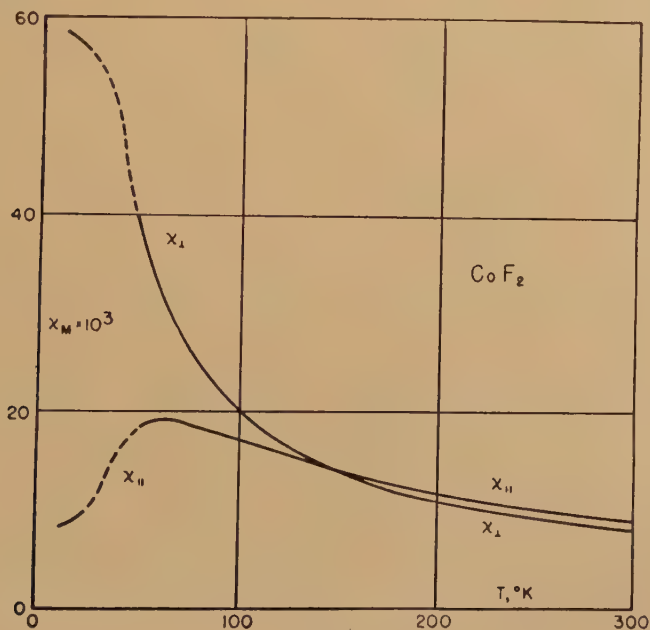
Molal magnetic susceptibilities of FeF_2 parallel and perpendicular to the c -axis of the crystal. (After Stout and Matarrese 1953.)

Fig. 12



(a)

Molal magnetic anisotropy of CoF_2 . $\chi_{||}$ and χ_{\perp} are molal susceptibilities parallel and perpendicular to the c -axis. (After Stout and Matarrese 1953.)

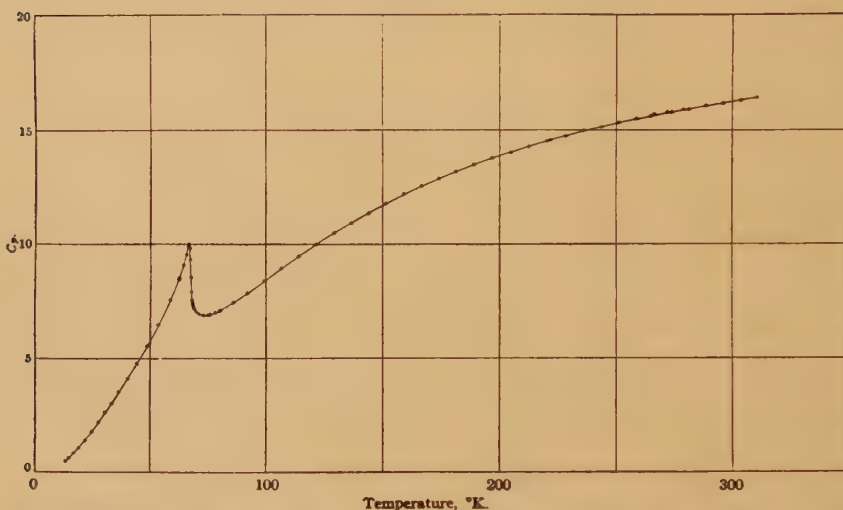


(b)

Molal magnetic susceptibilities of CoF_2 parallel and perpendicular to the c -axis of the crystal. (After Stout and Matarrese 1953.)

crystal suspended perpendicular to the (110) plane in one case and parallel to the tetragonal axis in another case. In the former case they observed that, unlike the other isomorphous fluorides, the susceptibility of NiF_2 at room temperature was greater perpendicular to the tetragonal axis than parallel to it and the difference between the perpendicular and parallel molal susceptibilities rose gradually from 1.102×10^{-4} at 301.15°K to 1.890×10^{-4} at 90.07°K . Below 73.2°K their measurements indicate that the crystal is spontaneously magnetized along the $\langle 100 \rangle$ directions, with a permanent moment whose magnitude is about $350 \text{ erg gauss}^{-1} \text{ mole}^{-1}$. Neutron diffraction measurements by Erickson, referred to in the preceding section, have indicated that in the ordered alignment the spins are inclined at an

Fig. 13



Heat capacity in calories per degree per mole of manganese fluoride. (After Stout and Adams 1942.)

angle of 10° to the tetragonal axis. If one assumes that the cocking of one sublattice is in the $[110]$ direction and that of the other sublattice at right angles in the $[1\bar{1}0]$ direction, then there is a net moment in the $[100]$ direction. The authors report that the moment of $350 \text{ erg gauss}^{-1} \text{ mole}^{-1}$, which is 3% of the saturation moment of the nickel ions, would on such a model correspond to a cocking of 2.5° .

We now turn to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Detailed measurements of the susceptibility of this substance have been made by van den Handel, Gijssman and Poullis (1952). As mentioned in § 1, there is the phenomenon of 'flopping' of spins in this substance and a consequent change in susceptibility. These were actually observed. Friedberg (1952) measured the specific heat of this substance and showed that only two-thirds of the total excess entropy, namely $(2/3) R \ln 2$, is obtained below

the Néel point, the remaining third being distributed above it. The Weiss approximation should therefore be poor for this substance.

A number of metals have also been investigated, but the experimental results are somewhat unrelated among themselves. In α -manganese, for instance, a small hump in the specific heat curve was observed by Shomate (1945) between 90° and 100°K , in agreement with the result of neutron diffraction, namely that the Néel point is at 100°K , though the hump is apparently too small for an order-disorder transition. On the other hand, the susceptibility measured by Shimizu (1930), Grube and Winkler (1936) and Bates and Pantulu (1935, amorphous manganese) above room temperature and by Serres (1938) between -200°C and 600°C showed no anomaly except in one example reported by Serres which showed a maximum at -100°C (173°K). These measurements show a slowly decreasing susceptibility above room temperature and thus indicate that the Néel point is in the range of low temperatures, if it exists at all, contrary to Néel's suggestion referred to in § 1. Ashworth (1936) observed a λ -anomaly in the specific heat curve at 350°C , while Armstrong (1950) observed no anomaly. In Cr, the Néel point predicted from neutron data is 200°C (473°K), but the susceptibility measurements due to Bates and Baqi (1936) between 100°K and 600°K and those due to Söchtig (1940) and McGuire and Kriessman (1952) at liquid oxygen or nitrogen temperature and above room temperature show that the susceptibility increases (rather than decreases) slowly with rising temperature, indicating that the Néel point is in the high temperature region, though the data are apparently not sufficient to give a definite conclusion. Armstrong (1950) has, however, observed a slight change in slope of the specific heat curve in the neighbourhood of 200°C . Fine, Greiner and Ellis (1951) observed an anomaly in Young's modulus at 121°K , and in this and in other properties at 37°C . Weertman, Burk and Goldman (1952), however, found no anomaly in the specific heat at the former temperature. Pursey (1952) also observed an anomaly in Young's modulus and rigidity at the latter temperature, which is close to the Néel temperature of Cr_2O_3 , 38°C . The former authors (Fine, etc.) report, however, that they used 99.8% pure Cr which was annealed at 1400°C in purified helium; the oxygen content was believed to be 0.05%.

At this place, it may be convenient to refer briefly to the band-theoretical treatment of antiferromagnetism put forward by Matsubara (1953) and Lidiard (1953, 1954). Following Slater's idea (Slater 1951), Matsubara starts with the assumption that the Hartree-Fock potential for electrons with $+$ spin is different from that for electrons with $-$ spin owing to the presence of an antiferromagnetic superstructure and of exchange interaction. The energy band for each spin is then shown to split into two, the difference between the two kinds of Hartree-Fock potential being the measure of this splitting. The electrons with positive spins in the lower band of the positive spins prefer to be on atoms of one sublattice, and those in the higher band prefer to be on atoms of the other

sublattice, while the preference is reversed for electrons with negative spin in the band of the negative spins. The bands are then filled with electrons and density matrices calculated for the electrons with positive and negative spins respectively. It is proved that, under a certain condition for the exchange integral, which is not a sufficient condition to eliminate the possibility of ferromagnetism appearing, the picture for such antiferromagnetism is consistent. Interesting results obtained are that the mean magnetic moment of the atoms can be predicted to be small and that the specific heat anomaly at the Néel point is also small. In fact, Matsubara could show that the observed values of these quantities in Mn are related to each other by his theory in a consistent way. Lidiard follows the same line and remarks further that the susceptibility does not necessarily show any anomaly at the Néel point.

We shall once more return to the experiments. Of solid solutions of antiferromagnetic compounds with diamagnetic compounds, four examples, $\text{MnO}+\text{MgO}$, $\text{FeO}+\text{MgO}$ and $\text{CoO}+\text{MgO}$ (Bizette and Tsai 1943, Bizette 1946) and $\text{MnF}_2+\text{ZnF}_2$ (Corliss, Delabarre and Elliott 1950), are reported. In the MnO and MnF_2 examples, the Curie constant per Mn atom is always constant but Θ is found to change proportionally to the Mn concentration, as can be expected, since Θ should be proportional to the Weiss molecular field. The Néel point is displaced to lower temperatures and becomes less definite as the concentration of MnO decreases. In $\text{FeO}+\text{MgO}$, the data appear to be not so definite but the general tendency is the same. Solid solutions of two antiferromagnetic compounds have been investigated by Bizette (1946) with $\text{FeO}+\text{MnO}$ and by Bacon, Street and Tredgold (1953) with $\text{MnO}+\text{CoO}$. The Néel temperature varies linearly with the concentration of one of the constituents, as one would expect. But Θ does not so vary (table 2). The

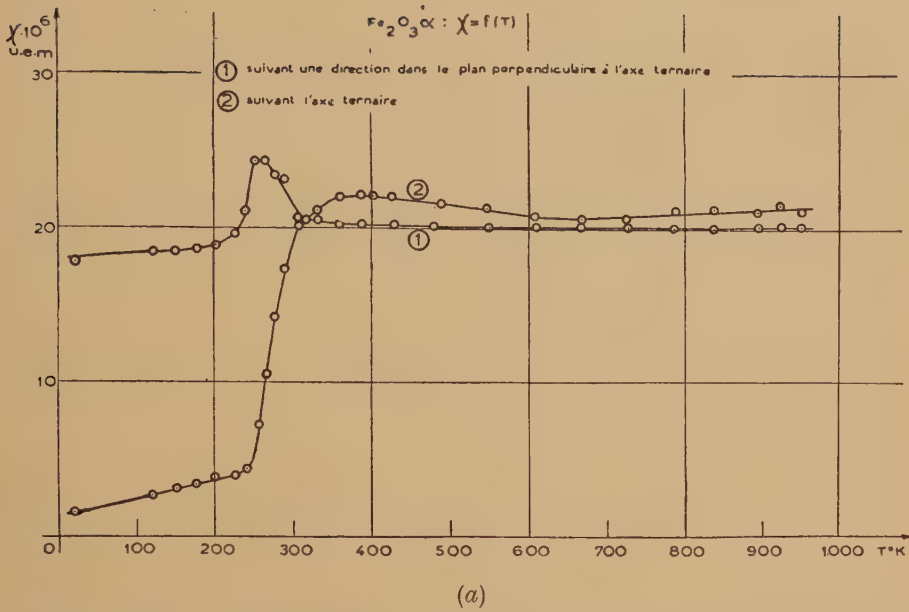
Table 2

MnO (σ)	CoO ($1-\sigma$)	T_N	Θ	C (per mole)
100%	0%	122°K	610°K	4.20
75	25	165	365	3.50
50	50	210	281	3.22
25	75	251	273	3.25
0	100	292	280	3.05

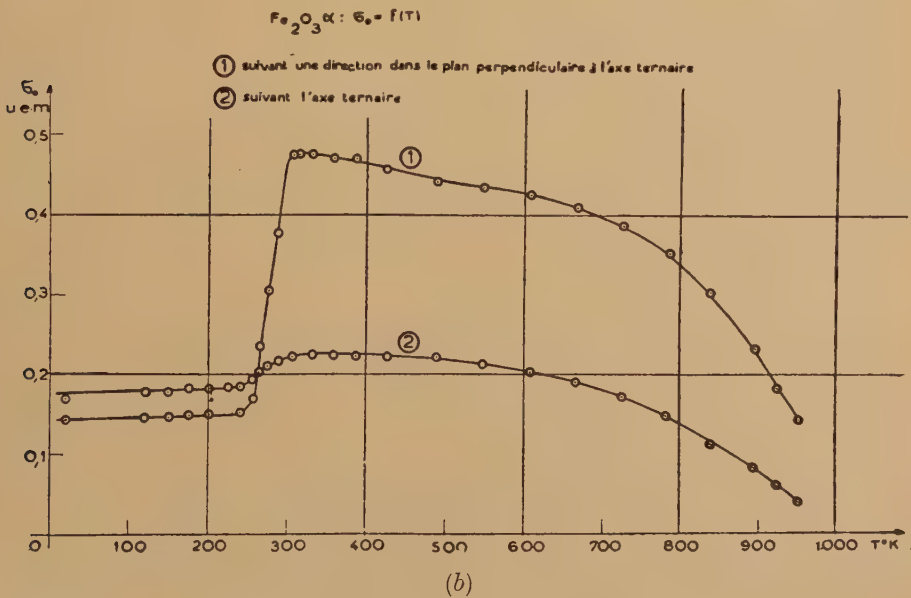
latter authors have made a reasonable assumption for the three types of superexchange coupling constant ($A_{ab}^2 = A_{aa}A_{bb}$, where A_{ab} , for instance, is the Weiss field constant for atoms a arising from atoms b , or vice versa) and derived the following formula for the susceptibility:

$$\chi = \frac{[\sigma C_a + (1-\sigma)C_b] + \sigma(1-\sigma)D/T}{T + [\sigma\Theta_a + (1-\sigma)\Theta_b] - \sigma(1-\sigma)E/T},$$

Fig. 14



Susceptibility of alpha hematite. Curve 1: along a direction in the plane perpendicular to the trigonal axis, curve 2: along the trigonal axis. (After Néel and Pauthenet 1952.)



Spontaneous magnetization of alpha hematite. Curve 1: along a direction in the plane perpendicular to the trigonal axis, curve 2: along the trigonal axis. (After Néel and Pauthenet 1952.) σ_0 is written as M_s in the text.

where σ is the concentration of the a atoms, C_a and C_b are the Curie constants for the pure compounds and D and E are constants. They found, however, that this formula does not accord well with experiment.

There are other substances which show more or less antiferromagnetic characteristics as well as ferromagnetic characteristics. Pyrrhotite, FeS, and CrS are antiferromagnetic when the composition is stoichiometric, but becomes ferromagnetic when an excess of sulphur is added; α -Fe₂O₃ would probably be antiferromagnetic if the crystal were perfect, but it shows a feeble ferromagnetism in actuality; MnBi and MnAs change from ferromagnetic to antiferromagnetic at a certain temperature; alkaline earth metal manganites and cobaltites are antiferromagnetic but become ferromagnetic when quadrivalent Mn-ions are introduced, by adding, for instance, LaMnO₃, in a certain range of concentration of the latter. There are substances which have a Néel point in the neighbourhood of 1°K and show interesting behaviours in strong magnetic fields. We shall return to the latter substances in § 7.

We might say a few words about the properties of α -hematite, which have been reviewed by Néel (1953 a) together with those of pyrrhotite and other substances. Néel (1949) suggested a 'parasitic ferromagnetism' as the origin of its weak ferromagnetism, though quite what is meant by 'parasitic' is not entirely clear at present. The magnetization of this substance under high field strengths has been shown by Pauthenet (1952) to follow the law $M = M_s + \chi H$. When the field is applied perpendicular to the trigonal main axis, the susceptibility χ is almost constant over a wide range of temperature from 20°K to 950°K, while, when the field is applied along the trigonal axis, it drops to very small values below 20°C. These could be well understood if we assumed a high anisotropy energy along the trigonal axis, a negligible anisotropy energy in the basal plane above 20°C and a change of the sign of the anisotropy energy below 20°C; the spins would then turn freely in the basal plane above 20°C and would become perpendicular to a field applied perpendicular to the trigonal axis, as well as to the field applied parallel; this would give rise to a constant susceptibility χ_{\perp} . Below 20°C they would point along the trigonal axis and give rise to χ_{\perp} for the former field but χ_{\parallel} for the latter field. According to Pauthenet's experiments the saturation magnetization M_s for the parasitic ferromagnetism appears to consist of two parts: one is independent of the anisotropy energy of the antiferromagnetism and the other makes its appearance in the basal plane above 20°C for a perpendicular field, but both have the same Curie temperature which is common to the main antiferromagnetism, namely, 1000°K. Recent measurements of ferromagnetic resonance by Anderson and others (1954) confirm the second parasitic ferromagnetism but give no evidence of the first one. It is, however, very curious that the antiferromagnetism and the parasitic ferromagnetism possess the same Curie point and yet no common anisotropy energy for the first parasitic one nor any common direction of magnetization for both.

Alums of Fe, Mn and Cr have a Curie or Néel point at a fraction of one degree absolute, but it is not clear whether they are ferromagnetic or antiferromagnetic. Magnetic dipole-dipole coupling seems to play here a predominant role. We shall not discuss them in this article. Molecular oxygen crystals may perhaps be antiferromagnetic, but if so it is obscured by the presence of two polymorphic phase transitions in its solid state. Recent measurements of susceptibility by Kanda at Tohoku University (Kanda 1954) show that the susceptibility changes discontinuously at these transition points.

§ 4. THEORY OF THE SUSCEPTIBILITY AT LOW FIELD STRENGTHS

The theory of the susceptibility of antiferromagnetic substances based on the Weiss molecular field approximation was founded by Néel (1932, 1936, a, b), Bitter (1937) and van Vleck (1941). An account of this theory will be given here, together with the extensions made by subsequent workers.

The Dirac formalism shows that exchange interactions of the Heisenberg type are equivalent to an interatomic potential

$$V_{ij} = -\frac{1}{2}J[1 + 4\mathbf{S}_i \cdot \mathbf{S}_j], \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where \mathbf{S}_i and \mathbf{S}_j are, respectively, the spin angular momentum vectors of atoms i and j measured in units of \hbar and J is the exchange integral. In ferromagnetism J is positive and denotes the coefficient of direct exchange coupling between neighbouring atoms whose electron clouds overlap with each other to some extent, if we assume Heisenberg's theory of ferromagnetism to be applicable. In antiferromagnetism, however, J is negative and denotes, in the case of compounds, predominantly the coefficient of indirect exchange coupling or superexchange coupling, that is, the coupling via the intermediary of a negative ion such as O^{--} (Anderson 1950 a); however in this case too we have the interaction of the same form as (4.1) (see §8). The superexchange is the strongest between those atoms which lie on opposite sides of the negative ion, since then one of the p-orbitals (2p in the case of O^{--}) contributes to it.

We assume that J is the same for all the interacting neighbours, z in number, and replace the sum over them, $\sum_j \mathbf{S}_j$, by $z\langle \mathbf{S}_j \rangle$, where $\langle \mathbf{S}_j \rangle$ means the statistical average of \mathbf{S}_j over the sublattice to which j belongs. Then the potential energy of the atom i is given as follows, apart from an additive constant :

$$V_i = \sum_j V_{ij} = -2Jz\langle \mathbf{S}_j \rangle \cdot \mathbf{S}_i. \quad . \quad . \quad . \quad . \quad (4.2)$$

We assume further that the Landé g -factor is isotropic, that is, it does not depend on the direction of the spin with respect to the crystal orientation ; this assumption will be removed later. The magnetic moment of an individual atom is then $\mu = -g\mu_B \mathbf{S}$, and we have

$$V_i = -2Jzg^{-2}\mu_B^{-2}\langle \mu_j \rangle \cdot \mu_i = -\mathbf{H}_{ej} \cdot \mu_i, \quad . \quad . \quad . \quad (4.3)$$

where

$$\mathbf{H}_{ej} = 2Jzg^{-2}\mu_B^{-2}\langle \mu_j \rangle \quad (J < 0) \quad . \quad . \quad . \quad (4.4)$$

this quantity being the exchange 'magnetic field' acting on atom i which results from the sublattice j . Another assumption we make in the following is that the whole lattice is divided into two similar sublattices, of which one possesses on each of its lattice points the spin of positive direction and the other the spin of negative direction. The existence of antiferromagnetic ordering has not yet been proved from first principles, except for the special model of a two-dimensional Ising system with a suitable lattice type (Onsager 1944, Husimi and Syozi 1950 and Syozi 1950), but all the experimental evidence shows that it does exist. There are cases where we have four or more sublattices, but we shall at first confine ourselves to the case of two sublattices, more complicated structures being reviewed at the end of this paragraph.

The exchange field acting on each spin of the positive lattice results from the negative lattice and also from other spins of the positive lattice; the importance of the latter has been emphasized by Néel (1948) and Anderson (1950 b). So we may put

$$\mathbf{H}_e^+ = -\alpha \langle \boldsymbol{\mu}^- \rangle - \gamma \langle \boldsymbol{\mu}^+ \rangle, \quad . \quad . \quad . \quad . \quad . \quad (4.5)$$

and similarly,

$$\mathbf{H}_e^- = -\alpha \langle \boldsymbol{\mu}^+ \rangle - \gamma \langle \boldsymbol{\mu}^- \rangle, \quad . \quad . \quad . \quad . \quad . \quad (4.6)$$

where α and γ are constants. If N is the number of magnetic atoms per unit volume, the magnetizations of the two sublattices are $\mathbf{M}^+ = (\frac{1}{2}N) \langle \boldsymbol{\mu}^+ \rangle$ and $\mathbf{M}^- = (\frac{1}{2}N) \langle \boldsymbol{\mu}^- \rangle$ so that (4.5) and (4.6) can be written

$$\mathbf{H}_e^+ = -A \mathbf{M}^- - \Gamma \mathbf{M}^+, \quad . \quad . \quad . \quad . \quad . \quad (4.7)$$

$$\mathbf{H}_e^- = -A \mathbf{M}^+ - \Gamma \mathbf{M}^-, \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

where

$$A = 2\alpha/N, \quad \Gamma = 2\gamma/N. \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

In the case where there is no external field, \mathbf{M}^+ and \mathbf{M}^- are antiparallel to each other, so long as A is positive and Γ is not too large. (If $\Gamma > A > 0$, each sublattice will divide itself into further sublattices with antiparallel spins.) We shall denote the common direction of \mathbf{M}^+ and \mathbf{M}^- by Δ . If there is an external field \mathbf{H} , they will be tilted to each other, and a convenient way of defining Δ may be to take it as the direction of $\mathbf{M}^+/M^+ - \mathbf{M}^-/M^-$, as done by Gorter and Haantjes (1952). This direction coincides with that of $\mathbf{M}^+ - \mathbf{M}^-$ so long as the angle between \mathbf{M}^+ and $-\mathbf{M}^-$ is small or the lengths of these two vectors are about the same.

It is evident from (4.1) that the direction Δ cannot be determined when there is no external field. The situation is the same as in ferromagnetism. We need the anisotropy energy to fix the direction of the magnetizations. In the ferromagnetic case, the direction of the magnetization is fixed along the preferred axis and a strong field is necessary to make it deviate from it. In the antiferromagnetic case, we expect the same situation, but the necessary field is even stronger, for the energy relative to the external field, $-\frac{1}{2}\chi H^2$, is much smaller than that for the ferromagnetic case, namely, $-\mathbf{H}\mathbf{M}$. Another difference in these two cases is that, if there

is no anisotropy energy, the magnetization vector is parallel to the applied field in the ferromagnetic case while the magnetization vectors of the two sublattices in the antiferromagnetic case are perpendicular to it. The latter follows from the fact that the susceptibility for the perpendicular position is the greatest and consequently the free energy is the lowest. We postpone the problem of the anisotropy energy to the next section, and wish here to discuss two special cases.

4.1. Δ parallel to \mathbf{H}

In this case, the magnitudes of the fields acting on the plus and minus spins are $|\mathbf{H} + \mathbf{H}_e^+|$ and $|\mathbf{H} + \mathbf{H}_e^-|$, respectively. The magnitudes of the thermal averages of μ^+ and μ^- , or the magnitudes of \mathbf{M}^+ and \mathbf{M}^- when multiplied by $\frac{1}{2}N$, are given by the standard theory of the molecular field approximation, and are

$$M^+ = \frac{1}{2}Ng\mu_B SB_S(y^+), \text{ with } y^+ = |\mathbf{H} + \mathbf{H}_e^+|Sg\mu_B/kT, \quad (4.10)$$

with a similar expression for the minus spin. Here

$$B_S(y) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} y - \frac{1}{2S} \coth \frac{y}{2S} \quad (4.11)$$

is the Brillouin function, which reduces to $\tanh y$ for $S = \frac{1}{2}$ and to the Langevin function $\coth y - 1/y$ for $S = \infty$. When there is no external field, (4.10) gives the same magnitude of the saturation magnetization, M_0 , for the two sublattices, which can be obtained from

$$M_0 = \frac{1}{2}Ng\mu_B SB_S(y_0), \text{ with } y_0 = (A - \Gamma)M_0Sg\mu_B/kT. \quad (4.12)$$

Here (4.7) and (4.8) have been used. M_0 is a decreasing function of temperature as in the case of ferromagnetism and vanishes at the critical point, or the Néel point, given by

$$T_N = \frac{1}{2}C(A - \Gamma), \quad (4.13)$$

where

$$C = Ng^2\mu_B^2 S(S+1)/3k \quad (4.14)$$

is the Curie constant.

To derive (4.13), we assume y_0 to be small and replace $SB_S(y_0)$ by $\frac{1}{3}(S+1)y_0$ and have from (4.12)

$$M_0 = (C/2T)(AM_0 - \Gamma M_0), \quad (4.15)$$

from which (4.13) follows at once.

The susceptibility above the Néel point can be written in the form

$$\chi = \frac{C}{T + \Theta}, \text{ with } \Theta = \frac{1}{2}C(A + \Gamma). \quad (4.16)$$

To derive this, we assume y^+ and y^- to be small and have from (4.10)

$$M^+ = \frac{C}{2T}(H - AM^- - \Gamma M^-), \text{ etc.} \quad (4.17)$$

since \mathbf{M}^+ and \mathbf{M}^- are both parallel to \mathbf{H} in the paramagnetic region. Solving this equation, we obtain $M^+ = M^-$, and, putting $M^+ + M^- = \chi H$, we obtain (4.16).

The susceptibility below the Néel point can be calculated by expanding $SB_s(y^+)$ in powers of H and retaining the first order term. It is essential here to assume that \mathbf{H}_e^+ and \mathbf{H}_e^- are respectively parallel and antiparallel to \mathbf{H} in order to obtain a consistent solution; otherwise, except in the case where they are equal in magnitude and make the same angle with \mathbf{H} , as we shall see below, (4.10) cannot be solved. We have $M^+ - M_0 = M_0 - M^-$ and

$$\chi_{||} = \frac{M^+ - M^-}{H} = \frac{3SB_s'(y_0)}{S+1} C \left/ \left[T + \frac{1}{2}(A+T)C \frac{3SB_s'(y_0)}{S+1} \right] \right. \quad (4.18)$$

This susceptibility vanishes at $T=0$, increases with rising temperature, and reduces to (4.16) above the Néel point.

4.2. Δ perpendicular to \mathbf{H}

In this case \mathbf{M}^+ and \mathbf{M}^- have the same magnitude and incline symmetrically to \mathbf{H} . The torque on, say, \mathbf{M}^+ must vanish:

$$|\mathbf{M}^+ \times (\mathbf{H} + \mathbf{H}_e^+)| = |\mathbf{M}^+ \times \mathbf{H} - A \mathbf{M}^+ \times \mathbf{M}^-| = M^+ H \cos \phi - A M^{+2} \sin 2\phi = 0,$$

from which we have

$$2M^+ \sin \phi = H/A, \quad \dots \dots \dots (4.19)$$

where ϕ is the angle which \mathbf{M}^+ makes with Δ . The left-hand side of (4.19) is the magnitude of the total magnetization, so that the susceptibility is

$$\chi_{\perp} = \text{constant} = 1/A. \quad \dots \dots \dots (4.20)$$

(4.20) and (4.16) give the same susceptibility at $T=T_N$.

Comparison with experiment. The general features of (4.16), (4.18) and (4.20) agree well with the experiments mentioned in § 3, if we understand by parallel and perpendicular susceptibilities those which correspond to \mathbf{H} being parallel and perpendicular, respectively, to the axis of easy magnetization. Two quantities here are of particular importance: the ratio of χ at $T=0$ to χ at $T=T_N$ in powdered specimens and the ratio of Θ to T_N .

In a powdered specimen of a substance with one preferred axis of magnetization, this axis is distributed in random directions in the specimen. One can decompose the external field acting on each individual crystallite into components parallel and perpendicular to the corresponding preferred axis and apply the result obtained above. The resulting averaged susceptibility is

$$\chi_p = \frac{1}{3} \chi_{||} + \frac{2}{3} \chi_{\perp}. \quad \dots \dots \dots (4.21)$$

Therefore the ratio $\chi_p(T=0)/\chi_p(T=T_N)$ is $\frac{2}{3}$ because $\chi_{||}$ vanishes at $T=0$, χ_{\perp} is constant and $\chi_{||} = \chi_{\perp}$ at $T=T_N$. Experimental values for this ratio are in the neighbourhood of $\frac{2}{3}$ (0.69 for MnO) but usually greater (see table 1). This may be attributed to the following reasons: incorrectness of the Weiss approximation for χ at $T=T_N$, existence of more than two sublattices, effect of anisotropy energy and anisotropy of the g -factor, etc. Li (1951) investigated the first point for the simple cubic lattice with spin $\frac{1}{2}$ by taking account of the local order of the spin

arrangement but neglecting the interaction among atoms of the same sublattice (see § 13). He obtained 0.769 for the ratio and also the result that $T_N = 2.00 |J|/k$, while our result (4.13) yields $T_N = \frac{1}{2} z |J|/k = 3 |J|/k$ for $\Gamma = 0$. Kanamori and Motizuki (1953, unpublished) applied the same method to the body-centred cubic lattice and obtained 0.723. Li gave for this case the Néel point only, which was $T_N = 3.18 |J|/k$, while (4.13) gives $T_N = 4 |J|/k$. We see that the value of the ratio is increased and the Néel temperature lowered when we go to a higher approximation. As regards the existence of more than two sublattices, the case of MnO_2 might be cited. The powder susceptibility of this substance measured by Bizette and Tsai (quoted in Bizette 1951) shows the ratio of about 0.9. The neutron diffraction experiment (see § 2) reveals that the spins are in the plane perpendicular to the tetragonal axis and form two uncorrelated sets of antiparallel arrangement, one being formed with corner atoms only and the other with body-centred atoms only, and that the direction of the magnetization in one set is possibly at right angles to that of the other set. If we assume an interaction between these two sets, 1 and 2, and denote the coefficient of the corresponding molecular field as Γ' , we have in place of (4.17) the following equations:

$$M_1^\pm = \frac{C}{4T} (H - A M_1^\mp - \Gamma M_1^\pm - \Gamma' M_2^+ - \Gamma' M_2^-),$$

$$M_2^\pm = \frac{C}{4T} (H - A M_2^\mp - \Gamma M_2^\pm - \Gamma' M_1^+ - \Gamma' M_1^-).$$

Summing up these four equations we obtain the total magnetization $M_1^+ + M_1^- + M_2^+ + M_2^-$. Then dividing it by H we obtain for the susceptibility above the Néel temperature

$$\chi = \frac{C}{T + C(A + \Gamma + 2\Gamma')/4}.$$

The Néel temperature can be obtained by putting all the M 's equal in magnitude to each other but taking the signs of the plus and minus magnetizations to be opposite. Then we have $T_N = C(A - \Gamma)/4$, in place of (4.13). The susceptibility at the Néel temperature is thus $2/(A + \Gamma')$. This gives at the same time the susceptibility for a field parallel to the tetragonal axis below the Néel temperature. To discuss the susceptibility for a field perpendicular to the tetragonal axis, we may suppose the field to be applied along the direction of the magnetization of one of the two sets, thus perpendicular to the other set. At absolute zero, the first set will contribute nothing to the susceptibility, while the second set will give rise to a susceptibility of magnitude $1/A$, just as in the simple case discussed before. The powder susceptibility at absolute zero is therefore given by

$$\chi_p = \frac{1}{3} \frac{2}{A + \Gamma'} + \frac{2}{3} \frac{1}{A} = \frac{2}{3(A + \Gamma')} \left(2 + \frac{\Gamma'}{A} \right).$$

The ratio in question is thus $(2 + \Gamma'/A)/3$, which is greater than $\frac{2}{3}$ if Γ' is positive. The argument here given is due to Yosida (1953).

To discuss the effect of the anisotropy energy on the ratio in question, we might call attention to the formula (5.10) to be derived later. If the anisotropy constant K is large, the perpendicular susceptibility is no longer constant with respect to the direction of the applied field and the simple formula (4.21) does not rigorously hold. If nevertheless we apply this formula and take as χ_{\perp} the value given by (5.8), which applies when Δ is along the easy axis and the field is perpendicular to it, and in which $K/2M_0^2$ should be independent of temperature, we obtain a ratio smaller than $\frac{2}{3}$, since χ_{\parallel} is unaffected by the anisotropy energy. In the majority of actual substances, however, in which the exchange field is much greater than the anisotropy field, such an effect should be negligible. The last of the possible reasons, that is, the effect of the anisotropic g -factor, will be discussed at the end of this section.

We now come to the ratio Θ/T_N . (4.13) and (4.16) give

$$\Theta/T_N = (A + \Gamma)/(A - \Gamma). \quad . \quad . \quad . \quad . \quad (4.22)$$

This is equal to 1 if $\Gamma=0$ but greater than 1 if $\Gamma>0$. Experimental values for this ratio can be obtained from table 1 and are usually greater than 1. According to (4.22) the ratio Θ/T_N could have any value however large, but this is not actually the case, since we are not always allowed to confine ourselves to the case of two-sublattices. In principle, we have to consider a number of possible superstructures and to compare the corresponding free energy values before applying (4.22). The model of two-sublattices would be valid only for a limited range of the relative values of A and Γ . Arguments of this kind have been developed by Anderson (1950 b, see also van Vleck 1951). The result, for instance, for the case of MnO is as follows. The structure of MnO found by neutron diffraction experiments (fig. 1) is stable only when $A > \frac{3}{4}\Gamma$, if we understand by A the coefficient of the coupling between those neighbours which lie at opposite sides of an oxygen ion and by Γ that between geometrically nearest neighbours. Otherwise another structure becomes more stable. For the former structure, which possesses four sets of antiparallel alignment, we can derive

$$\Theta = \frac{1}{4}(A + 3\Gamma), \quad T_N = \frac{1}{4}A; \quad \Theta/T_N = (A + 3\Gamma)/A.$$

These relations can be obtained by noticing that (4.15) and (4.17) are replaced in this case by

$$M_0 = \frac{C}{4T} A M_0 \quad \text{and} \quad M^+ = \frac{C}{4T} (H - A M^+ - 3\Gamma M^+), \text{ etc.}$$

The maximum value of the ratio Θ/T_N is therefore obtained for $A = \frac{3}{4}\Gamma$ and is 5, which is close to that observed in MnO. For other details of this kind of consideration, the reader may consult Anderson's or van Vleck's original articles and a contribution by Smart (1953).

Also the crudeness of the molecular field theory might be responsible for the difference between the actual Θ/T_N and its value 1 predicted for

$\Gamma=0$ from that theory. More elaborate statistical theory, such as the Bethe-Peierls-Weiss method employed by Li (1951) predicts generally a curvature for the plot of $1/\chi$ versus temperature above the Néel point. But the theory cannot be trusted to separate this statistical effect from the effect of the next nearest neighbour interaction. (See also § 17.)

Anisotropic g -factor. We have so far assumed that g is a scalar. In some substances, the g -factor depends on the orientation of the spins relative to the crystalline axes. This occurs when there is a spin-orbit interaction and a splitting of the electronic energy level in the crystalline electric field, the theory of which will be given in § 9. In such a case, the g -factor is a tensor and moreover may depend on temperature. The principal axes of the g -tensor may be different from the crystallographic axes for individual atoms, since the symmetry axes of the crystalline field for a given atom does not necessarily coincide with the latter axes. If there is more than one kind of g -tensor in the crystal, the problem becomes complicated, since we have to treat more than two sublattices and to quantize the spins separately on each of the sublattices in a given external field and in the exchange field, which itself may be different for the different sublattices of the plus or minus spins only. This situation has not been clearly analysed even in the approximation of the molecular field, though actually the substance $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ corresponds to this case.

We shall simply assume that there is only one g -tensor in the lattice. (If not, the different g -tensors may be thought to be replaced by an average g -tensor.) Then the principal axes of this tensor must coincide with the crystalline axes in the case of orthorhombic or tetragonal or cubic lattices. We shall denote the corresponding principal values of the g -tensor by g_1, g_2, g_3 . The reduction of this g -tensor to a scalar g -factor is then a simple matter. The interaction between the external field \mathbf{H} and the spins is represented by the Hamiltonian $\mu_B \sum_i \mathbf{S}_i g \mathbf{H}$, and this can be replaced by $\mu_B g \sum_i \mathbf{S}_i \mathbf{H}'$ if we define \mathbf{H}' by $g\mathbf{H} = g\mathbf{H}'$, or, in terms of the principal values of g , by

$$g_1 H_1 = g H_1', \quad g_2 H_2 = g H_2', \quad g_3 H_3 = g H_3', \quad \dots \quad (4.23)$$

where H_1, H_1' , etc. mean the components of \mathbf{H} and \mathbf{H}' along the principal axes. In other words, we can use the fictitious external field \mathbf{H}' in place of the real external field \mathbf{H} and treat the g -factor as a scalar.

In particular, if we are interested in the susceptibility, for instance, along the axis 1, that is, the susceptibility for the field applied along the axis 1, we have only to multiply the susceptibility $\chi(\chi_{\parallel}$ or χ_1 below the Néel point) obtained in the fictitious (g, \mathbf{H}') -system by $(g_1/g)^2$ to obtain the real susceptibility, because the susceptibility can be obtained by differentiating the free energy twice with respect to the component of the field and each time when the free energy is differentiated we have the factor g_1 for the real field but g for the fictitious field. This is because the free energy is a function of the interaction Hamiltonian given above.

We may take the axis 1 as the preferred axis of magnetization and axes 2 and 3 perpendicular to it. Then the powder susceptibility (the real one) is given by

$$\chi_p = \frac{1}{3} \{ (g_1/g)^2 \chi_{11} + (g_2/g)^2 \chi_{22} + (g_3/g)^2 \chi_{33} \}, \quad (4.24)$$

instead of $\frac{1}{3} \chi_{11} + \frac{2}{3} \chi_{22}$. The ratio of $\chi_p(T=0)$ to $\chi_p(T=T_N)$ is therefore $(g_2^2 + g_3^2)/(g_1^2 + g_2^2 + g_3^2)$, which is not necessarily equal to $\frac{2}{3}$.

§ 5. THEORY OF THE SUSCEPTIBILITY AT MODERATELY HIGH FIELDS

We now proceed to the case where the applied field is high but not so high as to decouple the exchange interaction between magnetic atoms. We conveniently divide the subject under the following headings.

5.1. Anisotropy Energy

We shall introduce here the anisotropy energy in a phenomenological way. Let the direction cosines of $\langle \mathbf{S}^+ \rangle$, or of \mathbf{M}^+ , be α_+ , β_+ , γ_+ , with a similar notation for negative sign, and those of Δ , the direction of $\mathbf{M}^+ - \mathbf{M}^-$, be α , β , γ . We shall always suppose an isotropic g -factor and consequently \mathbf{M}^\pm to be constant multiples of $\langle \mathbf{S}^\pm \rangle$. If otherwise, \mathbf{M} 's and \mathbf{H} are to be primed and the methods mentioned at the end of the last section are to be applied. We introduce the anisotropy energy in the simplest form:

$$\text{Uniaxial case: } E_a = -\frac{1}{2} K (\gamma_+^2 + \gamma_-^2) \approx -K \gamma^2. \quad (5.1)$$

Biaxial or orthorhombic case:

$$E_a = \frac{1}{2} K_1 (\beta_+^2 + \beta_-^2) + \frac{1}{2} K_2 (\gamma_+^2 + \gamma_-^2) \approx K_1 \beta^2 + K_2 \gamma^2. \quad (5.2)$$

$$\text{Cubic case: } E_a = -\Sigma_{\pm} \frac{1}{4} K (\alpha_{\pm}^4 + \beta_{\pm}^4 + \gamma_{\pm}^4) \approx -\frac{1}{2} K (\alpha^4 + \beta^4 + \gamma^4). \quad (5.3)$$

In the uniaxial case, one can think of other expressions such as

$$K'(\alpha_+ \alpha_- + \beta_+ \beta_-) + K'' \gamma_+ \gamma_-,$$

but this reduces to (5.1) when $(\alpha_+ + \alpha_-)^2$, etc. are neglected compared with unity, since \mathbf{M}^+ and \mathbf{M}^- are almost antiparallel to each other. A similar remark applies to the other cases. As in ferromagnetism, we may assume that the anisotropy energy is small compared with the exchange energy. We therefore assume that the magnitudes of the plus and minus magnetization vectors are not influenced by the anisotropy energy. Then we can introduce an 'anisotropy magnetic field' through the equation

$$\delta E_a = -\mathbf{H}_a^+ \cdot \delta \mathbf{M}^+ - \mathbf{H}_a^- \cdot \delta \mathbf{M}^-, \quad (5.4)$$

where δ denotes an arbitrary variation of the corresponding quantity and it is understood that the magnitudes of the plus and minus magnetization vectors, \mathbf{M}^+ and \mathbf{M}^- , are kept constant, though they can change their orientations. Applying (5.4) to the uniaxial case, we have

$$\begin{aligned} \delta E_a &= -K (\gamma_+ \delta \gamma_+ + \gamma_- \delta \gamma_-) \\ &= -\Sigma_{\pm} (H_{ax}^{\pm} \delta \alpha_{\pm} + H_{ay}^{\pm} \delta \beta_{\pm} + H_{az}^{\pm} \delta \gamma_{\pm}) M^{\pm}, \end{aligned}$$

so that

$$H_{ax}^{\pm} = H_{ay}^{\pm} = 0, \quad H_{az}^{\pm} = (K/M^{\pm}) \gamma_{\pm} = (K/M_0) \gamma_{\pm}, \quad (5.5)$$

where we have put $M^+ = M^- = M_0$ at the last equality sign, M_0 being the value of M^+ for vanishing external field. In deriving (5.5) we have tacitly assumed that the variations of the direction cosines can take arbitrary values, but actually this is not the case because $\alpha_+^2 + \beta_+^2 + \gamma_+^2 = 1$. This condition introduces, however, an arbitrary additive anisotropy field parallel to each of the magnetization vectors, which is not important in constraining the direction of the latter.

In the biaxial and cubic cases, we obtain in a similar way the following anisotropy fields:

$$H_{ax}^\pm = 0, \quad H_{ay}^\pm = -(K_1/M_0)\beta_\pm, \quad H_{az}^\pm = -(K_2/M_0)\gamma_\pm, \quad . \quad . \quad (5.6)$$

$$H_{ax}^\pm = (K/M_0)\alpha_\pm^3, \quad H_{ay}^\pm = (K/M_0)\beta_\pm^3, \quad H_{az}^\pm = (K/M_0)\gamma_\pm^3. \quad . \quad (5.7)$$

We shall investigate two special cases.

5.2. The Case of Uniaxial Anisotropy with Positive K

In this case the magnetization vectors \mathbf{M}^+ and \mathbf{M}^- are normally in the direction of the axis of anisotropy, namely, the z -axis. When a field \mathbf{H} is applied along this direction, they change their magnitudes but do not deviate from that direction as long as the field strength is not higher than the critical field strength, H_c . In this case, the anisotropy energy evidently plays no role.

When, however, \mathbf{H} is applied perpendicular to that axis, we have a small correction to the perpendicular susceptibility due to the anisotropy energy. The torque acting on, say, \mathbf{M}^+ is

$$|\mathbf{M}^+ \times (\mathbf{H} + \mathbf{H}_e + \mathbf{H}_a)| = M^+ H \cos \phi - A M^{+2} \sin 2\phi - M^+ (K/M_0) \sin \phi \cos \phi, \\ (\cos \phi = \gamma_+ = -\gamma_-), \text{ which must vanish, so that}$$

$$2M^+ \sin \phi = \frac{H}{A + K/2M_0^2}.$$

The left-hand side of the equation is the magnitude of the induced magnetic moment, so that the susceptibility is given as

$$\chi_\perp = 1/(A + K/2M_0^2). \quad . \quad . \quad . \quad . \quad (5.8)$$

Similarly, we obtain the susceptibility χ_\perp when Δ is perpendicular and \mathbf{H} is parallel to the z -axis as follows:

$$\chi_\perp = 1/(A - K/2M_0^2). \quad . \quad . \quad . \quad . \quad (5.9)$$

For the general case, we may assume \mathbf{H} to be applied in the xz -plane and Δ also to be in this plane. It may be seen from the arguments given later in § 5.3 that Δ cannot deviate from this plane. We define angles $\theta_H, \psi, \theta_+, \theta_-$ and ϕ as indicated in fig. 15. We decompose \mathbf{H} into components parallel and perpendicular to Δ , $H_\parallel = H \cos \psi$ and $H_\perp = H \sin \psi$. The parallel component causes the magnitude of M^+ to change to $M_0 + \frac{1}{2}\chi_\parallel H_\parallel$ and the perpendicular component makes it deflect from Δ by an equal angle ϕ . We assume that the square of this angle can be neglected compared with 1, that is that $M_0^2 \gg \frac{1}{4}(\chi_\perp H_\perp)^2$, and also neglect

$\frac{1}{4}(\chi_{\parallel}H_{\parallel})^2$ compared with M_0^2 . In this approximation the equations of the balance of torque can be written as

$$(M_0 + \frac{1}{2}\chi_{\parallel}H_{\parallel})H \sin(\psi - \phi) - AM_0^2 \sin 2\phi + K \cos \theta_+ \sin \theta_+ = 0,$$

$$(M_0 - \frac{1}{2}\chi_{\parallel}H_{\parallel})H \sin(\psi + \phi) - AM_0^2 \sin 2\phi - K \cos \theta_- \sin \theta_- = 0,$$

where

$$\theta_+ = \psi - \theta_H - \phi, \quad \theta_- = \psi - \theta_H + \phi.$$

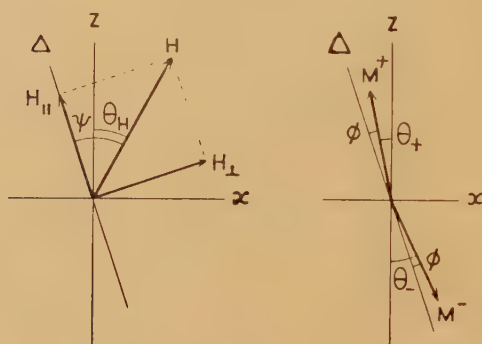
When we again neglect $\chi_{\perp}\chi_{\parallel}H_{\parallel}^2/4$ against M_0^2 and put $2M_0 \sin \phi = \chi_{\perp}H_{\perp}$, we obtain

$$\chi_{\perp} = 1/[A + (K/2M_0^2) \cos \{2(\psi - \theta_H)\}] \quad . \quad . \quad . \quad (5.10)$$

and

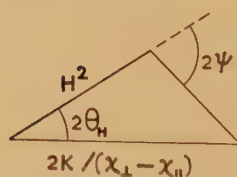
$$(\chi_{\perp} - \chi_{\parallel})H^2 \sin \psi \cos \psi = K \sin \{2(\psi - \theta_H)\}. \quad . \quad . \quad . \quad (5.11)$$

Fig. 15



Definition of angles.

Fig. 16



Geometrical representation of eqn. (5.12).

(5.10) agrees with (5.8) and (5.9) for the corresponding special cases, and (5.11) can be written in another form

$$\tan 2\psi = \frac{\sin 2\theta_H}{\cos 2\theta_H - (\chi_{\perp} - \chi_{\parallel})H^2/2K} \quad . \quad . \quad . \quad (5.12)$$

(5.12) gives ψ as a function of θ_H and H if the term in (5.10) dependent on K is neglected. A geometrical representation of this relation is shown in fig. 16.

An interesting result of the above calculation is a sudden change of the directions of magnetization in the case where \mathbf{H} is applied along the easy axis. From fig. 16 it can be seen that ψ is 0 or $\frac{1}{2}\pi$ according as $H < H_c$ or $H > H_c$ when $\theta_H = 0$, where

$$H_c = [2K/(\chi_{\perp} - \chi_{\parallel})]^{1/2}. \quad (5.13)$$

Here the K -dependent term in (5.10) is (and should be) neglected since it is of the order of $(\chi_{\perp} - \chi_{\parallel})H_c^2/4M_0^2$ and must be considered small compared with A , or the reciprocal of χ_{\perp} , in our approximation when H is of the order of H_c . A simpler derivation of (5.13) was given in § 1, comparing the values of the free energy at the parallel and perpendicular positions. Thus the direction of the magnetization turns at $H = H_c$ from the direction of the easy axis to that perpendicular to it. This phenomenon of flopping of spins was first predicted by Néel (1936 a) and was found by Gorter and his collaborators (1951) to occur actually in the crystal of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

Another result which follows from the arguments above is the field-dependence of the susceptibility. We shall now assume $H^2 \ll H_c^2$. The components of the magnetization induced in the directions parallel and perpendicular to Δ are $\chi_{\parallel}H \cos \psi$ and $\chi_{\perp}H \sin \psi$, respectively. ψ depends on H^2 through eqn. (5.12), so that the induced magnetization also depends on H^2 . (5.12) can be written in another form

$$\tan 2\theta = \frac{(\chi_{\perp} - \chi_{\parallel})H^2 \sin 2\theta_H}{2K - (\chi_{\perp} - \chi_{\parallel})H^2 \cos 2\theta_H} = \frac{H^2}{H_c^2} \sin 2\theta_H \left(1 - \frac{H^2}{H_c^2} \cos 2\theta_H\right)^{-1}, \quad (5.14)$$

where $\theta = \psi - \theta_H$ is the angle between Δ and the easy axis, and thus for $H^2 \ll H_c^2$ we have $\tan 2\theta = (H^2/H_c^2) \sin 2\theta_H$. The parallel and perpendicular components of the induced magnetization are therefore given approximately as

$$\begin{aligned} \chi_{\parallel}H \{\cos \theta_H - (H^2/2H_c^2) \sin \theta_H \sin 2\theta_H\}, \\ \chi_{\perp}H \{\sin \theta_H - (H^2/2H_c^2) \cos \theta_H \sin 2\theta_H\}, \end{aligned} \quad (5.15)$$

respectively. Here we have to take (5.8) for χ_{\perp} , if the anisotropy energy is not at all negligible, because $\psi - \theta_H$ is small. Now if we are interested in the component of the induced magnetization along the applied field, we have to multiply each of (5.15) by $\cos \psi$ and $\sin \psi$, respectively, and add them

$$\begin{aligned} \chi_{\parallel}H \cos^2 \psi + \chi_{\perp}H \sin^2 \psi \\ = H [\chi_{\parallel} \cos^2 \theta_H + \chi_{\perp} \sin^2 \theta_H + 2(\chi_{\perp} - \chi_{\parallel}) \sin^2 \theta_H \cos^2 \theta_H (H^2/H_c^2)]. \end{aligned}$$

The average of this expression over all possible crystal orientations yields the powder susceptibility

$$\chi_p = \frac{1}{3} \chi_{\parallel} + \frac{2}{3} \chi_{\perp} + \frac{4}{15} (\chi_{\perp} - \chi_{\parallel}) (H^2/H_c^2) = \frac{1}{3} \chi_{\parallel} + \frac{2}{3} \chi_{\perp} + \frac{2}{15K} (\chi_{\perp} - \chi_{\parallel})^2 H^2. \quad (5.16)$$

where $\alpha_H, \beta_H, \gamma_H$ are the direction-cosines of \mathbf{H} and the anisotropy energy is simplified as shown. We look for the minimum of this free energy expression subject to the condition $\alpha^2 + \beta^2 + \gamma^2 = 1$. The problem is the same as that of looking for the longest principal axis of the ellipsoid $F=1$ in the α, β, γ -space. We have only to solve the equation

$$\begin{vmatrix} \alpha_H^2 - \lambda & \alpha_H \beta_H & \alpha_H \gamma_H \\ \alpha_H \beta_H & \beta_H^2 + \kappa_1 - \lambda & \beta_H \gamma_H \\ \alpha_H \gamma_H & \beta_H \gamma_H & \gamma_H^2 + \kappa_2 - \lambda \end{vmatrix} = 0 \quad . \quad . \quad . \quad (5.20)$$

to obtain the stationary values of F , i.e.

$$\lambda^3 - (1 + \kappa_1 + \kappa_2) \lambda^2 + [(\kappa_1 + \kappa_2) \alpha_H^2 + \kappa_2 \beta_H^2 + \kappa_1 \gamma_H^2 + \kappa_1 \kappa_2] \times \lambda - \kappa_1 \kappa_2 \alpha_H^2 = 0, \quad . \quad . \quad . \quad (5.21)$$

where

$$\kappa_1 = 2K_1 / [(\chi_{\perp} - \chi_{\parallel}) H^2], \quad \kappa_2 = 2K_2 / [(\chi_{\perp} - \chi_{\parallel}) H^2]. \quad . \quad . \quad . \quad (5.22)$$

The lowest root of (5.21) is the desired one, and the corresponding direction α, β, γ can be calculated from the elements of the matrix of (5.20) after substituting this lowest root for λ .

By a simple calculation one can show that, when \mathbf{H} is in one of the coordinate planes, there is such a root which does not depend on the direction of \mathbf{H} . For instance, when \mathbf{H} is in the xz -plane, one gets a root $\lambda = \kappa_1$. We have therefore the possibility of a crossing of two of the roots when the direction of \mathbf{H} is varied in that plane. In the case of the xz -plane, it can be shown easily that the crossing occurs for the two lower roots along the hyperbola

$$\frac{H_x^2}{2K_1} - \frac{H_z^2}{2(K_2 - K_1)} = \frac{1}{\chi_{\perp} - \chi_{\parallel}}, \quad . \quad . \quad . \quad (5.23)$$

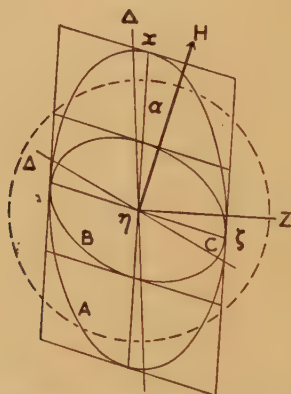
and that the magnetization direction α, β, γ changes abruptly when the field strength crosses over this hyperbola; this direction is confined in the xz -plane for field strengths inside the hyperbola but coincides with the y -direction for those outside the hyperbola. We shall call (5.23) the *critical hyperbola*. Its vertex evidently coincides with the critical value of H given by (5.13) if we put $K_1 = K$. When the applied field is in the xy -plane, we have a crossing of the two higher roots along an ellipse, but this does not interest us. For the yz -plane, there is no crossing. It can be said in general that for the applied field outside the xz -plane no abrupt change of the magnetization direction can occur.

The matter can be understood in another way by using a geometrical representation. We introduce oblique coordinate axes y, z, \mathbf{H} and their reciprocal axes η, ζ, x . (The reciprocal axes are those with which we are familiar in crystallography.) The ellipsoid $F = \text{constant}$ can be written with respect to these reciprocal axes as

$$K_1 \eta^2 + K_2 \zeta^2 + \frac{1}{2} (\chi_{\perp} - \chi_{\parallel}) H^2 x^2 = 1. \quad . \quad . \quad . \quad (5.24)$$

The longest principal axis of this ellipsoid is that required, and it determines the direction of the magnetization, Δ . Figure 17 represents the ellipsoid when \mathbf{H} is in the xz -plane. The semi-axial lengths, a , c , indicated in the figure and that along the η -axis, b , are, respectively the inverse square roots of $\frac{1}{2}(\chi_1 - \chi_{II}) H^2$, K_2 and K_1 . Therefore an increase in H flattens the ellipsoid along the x -axis and makes the principal axes rotate in some way. If \mathbf{H} is in the xz -plane, the ellipsoid is symmetrical with respect to this plane so that two of the principal axes lie in this plane and the remaining one is along the η -axis. With varying H the former two rotate in the xz - or $x\zeta$ -plane and change their lengths at the same time, while the latter one remains unchanged. For small H the longest principal axis is evidently that which is close to the x -axis, but as H increases a value is reached for which the principal axis along the η -axis becomes the longest, since $K_2 > K_1$ and hence $c < b$. This explains the sudden flopping of the spin direction mentioned above. If \mathbf{H} is in any other direction, nothing like this can occur, the longest principal axis changing its direction continuously with changing field intensity.

Fig. 17



The ellipsoid given by eqn. (5.24). The ellipse A represents the cross section of this ellipsoid with the xz -plane for $H > H_c$ and the ellipse B represents that for $H < H_c$. a and c represent semi-axial lengths, and the dotted circle represents the sphere of radius b which touches the ellipsoid at the η -axis. The field is applied in the xz -plane.

The critical hyperbola (5.23) was first derived by Gorter and Haantjes (1952) for absolute zero ($\chi_{II} = 0$) by a different method, and its existence in actual substances was proved by susceptibility measurements by van den Handel, Gijsman and Poulis (1952) for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. A simplified derivation described above, with a generalization to finite temperatures, is due to Nagamiya (1953, 1954). Gorter and Haantjes assumed an anisotropic Weiss field coefficient, namely $(-A_x M_x^-, -A_y M_y^-, -A_z M_z^-)$ for the exchange field \mathbf{H}_e^+ , but this is equivalent to our formulation as long as the applied field is small compared with

the exchange field so that the plus and minus magnetization vectors are almost antiparallel to each other. To see this equivalence, we write the free energy due to the exchange field as

$$\begin{aligned} & A_x M_x^+ M_x^- + A_y M_y^+ M_y^- + A_z M_z^+ M_z^- \\ &= A_x (M_x^+ M_x^- + M_y^+ M_y^- + M_z^+ M_z^-) + (A_y - A_x) M_y^+ M_y^- \\ & \quad + (A_z - A_x) M_z^+ M_z^-. \end{aligned}$$

The first term on the right-hand side represents the free energy corresponding to the isotropic Weiss field coefficient and the remaining terms represent the anisotropy energy, which can be written as

$$-K_1 \beta_+ \beta_- - K_2 \gamma_+ \gamma_-,$$

with K_1 and K_2 proportional to M_0^2 , if the plus and minus magnetizations are almost antiparallel and their magnitudes do not differ greatly from each other. Gorter and Haantjes treated also the case where the applied field is of the order of, or greater than, the exchange field. We do not consider this case here (but see § 7).

§ 6. ANTIFERROMAGNETIC RESONANCE

6.1. Theory

We have so far confined ourselves to static problems. To go over to the dynamical case, we have to set up the equation of motion. This can be done in an approximate way by extending Kittel's equation of motion, familiar in ferromagnetic resonance problems, which states that the rate of change in the angular momentum of the whole system is equal to the torque acting on the magnetization vector of that system. We apply this principle to each of the two sublattices of an antiferromagnetic crystal and have

$$\frac{1}{\gamma} \frac{d}{dt} \mathbf{M}^\pm = \mathbf{M}^\pm \times (\mathbf{H} + \mathbf{H}_e^\pm + \mathbf{H}_a^\pm), \quad \gamma = g\mu_B/\hbar. \quad (6.1)$$

We define

$$\mathbf{M} = \mathbf{M}^+ + \mathbf{M}^-, \quad \mathbf{M}' = \mathbf{M}^+ - \mathbf{M}^-. \quad (6.2)$$

Then, adding and subtracting the two equations (6.1) and utilizing the relation $\mathbf{H}_e^+ = -A\mathbf{M}^- - \Gamma\mathbf{M}^+$, etc. for the exchange fields, we obtain

$$\frac{1}{\gamma} \frac{d}{dt} \mathbf{M} = \mathbf{M} \times \mathbf{H} + \mathbf{M} \times \frac{1}{2} (\mathbf{H}_a^+ + \mathbf{H}_a^-) + \mathbf{M}' \times \frac{1}{2} (\mathbf{H}_a^+ - \mathbf{H}_a^-), \quad (6.3)$$

$$\frac{1}{\gamma} \frac{d}{dt} \mathbf{M}' = \mathbf{M}' \times (\mathbf{H} - A\mathbf{M}) + \mathbf{M} \times \frac{1}{2} (\mathbf{H}_a^+ - \mathbf{H}_a^-) + \mathbf{M}' \times \frac{1}{2} (\mathbf{H}_a^+ + \mathbf{H}_a^-). \quad (6.4)$$

In the ferromagnetic case we have only one equation of the form of (6.3) except that a single term $\mathbf{M} \times \mathbf{H}_a$ replaces the anisotropy terms, provided we neglect the demagnetizing field and also the damping term. Moreover, save for the anisotropy field term, the equation in the ferromagnetic case is a rigorous quantum-mechanical one, though the anisotropy term is more or less of a phenomenological nature (van Vleck 1950).

terms in (6.4), namely (6.6), can be entirely neglected compared with the first term in (6.4), since they are in the ratio $H_a : H_c$ as to their order of magnitude. If this term is not neglected, the treatment becomes complicated, except in one case, (6.1.1(a)) below, where the calculation is still quite simple. This term is therefore neglected except in this case.

The equation of small oscillation now comes out by use of (6.5) and (6.7) to be

$$\frac{1}{\gamma} \frac{d}{dt} \delta \mathbf{M} = -\mathbf{H} \times \delta \mathbf{M} + \begin{cases} -\frac{K_2 - K_1}{2M_0^2} (M_z' \delta M_y' + M_y' \delta M_z'), \\ +\frac{K_2}{2M_0^2} (M_x' \delta M_z' + M_z' \delta M_x'), \\ -\frac{K_1}{2M_0^2} (M_y' \delta M_x' + M_x' \delta M_y'), \end{cases} \quad (6.9)$$

$$\frac{1}{\gamma} \frac{d}{dt} \mathbf{M}' = -\alpha \frac{(\mathbf{M}' \cdot \mathbf{H})}{4M_0^2} \mathbf{M}' \times \delta \mathbf{M}' - A \mathbf{M}' \times \delta \mathbf{M}. \quad (6.10)$$

In these equations we have to substitute the static values of \mathbf{M} and \mathbf{M}' derived in § 5. We shall apply these equations to several special cases.

6.1.1. The Applied Field is Parallel to the x -axis

In this case we have to distinguish three cases: $H < H_c$, $H > H_c$, and $H = H_c$. At $H = H_c$ the axis of magnetization, that is, the direction of \mathbf{M}' turns in the xy -plane and the frequencies of the eigen-oscillations of the system vary with the angle through which it turns. For a given frequency of an applied oscillating field we can therefore expect a resonance to occur at $H = H_c$ if the range of those frequency variations cover this given frequency. We shall come to this case later.

(a) $H < H_c$. The vectors \mathbf{M} and \mathbf{M}' both point in the x -direction, so that (6.9) and (6.10) can be written as

$$\begin{aligned} \gamma^{-1} \delta \dot{M}_y &= H \delta M_z + (K_2/M_0) \delta M_z', \\ \gamma^{-1} \delta \dot{M}_z &= -H \delta M_y - (K_1/M_0) \delta M_y', \\ \gamma^{-1} \delta \dot{M}_y' &= \alpha H \delta M_z' + 2AM_0 \delta M_z, & + (K_2/2M_0^2) \chi_{11} H \delta M_z' + (K_2/M_0) \delta M_z, \\ \gamma^{-1} \delta \dot{M}_z' &= -\alpha H \delta M_y' - 2AM_0 \delta M_y, & - (K_1/2M_0^2) \chi_{11} H \delta M_y' - (K_1/M_0) \delta M_y. \end{aligned}$$

Terms written to the right of the vertical bar are due to (6.6) which has been neglected. If we take account of them, we cannot put $A = 1/\chi_{11}$, so that α should be $1 - A\chi_{11}$. Neglecting them for a moment, and taking δM_y , δM_z , $\delta M_y'$, $\delta M_z'$ proportional to $\exp(i\omega t)$, we obtain the determinantal equation

$$\begin{vmatrix} -i\omega/\gamma & H & 0 & K_2/M_0 \\ -H & -i\omega/\gamma & -K_1/M_0 & 0 \\ 0 & 2AM_0 & -i\omega/\gamma & \alpha H \\ -2AM_0 & 0 & -\alpha H & -i\omega/\gamma \end{vmatrix} = 0.$$

This reduces to

$$(\omega/\gamma)^4 - (\omega/\gamma)^2[(1+\alpha^2)H^2 + c_1 + c_2] + \alpha^2 H^4 - H^2(\alpha c_1 + \alpha c_2) + c_1 c_2 = 0, \quad (6.11)$$

where

$$c_1 = 2AK_1, \quad c_2 = 2AK_2. \quad (6.12)$$

We therefore have

$$\left(\frac{\omega}{\gamma}\right)^2 = \frac{1}{2}[(1+\alpha^2)H^2 + c_1 + c_2 \pm \{(1-\alpha^2)^2 H^4 + 2(1+\alpha)^2 H^2(c_1 + c_2) + (c_1 - c_2)^2\}^{1/2}]. \quad (6.13)$$

For the special case of $c_1 = c_2$ and absolute zero (where $\alpha = 1$), (6.13) reduces to

$$\omega/\gamma = (2AK)^{1/2} \pm H. \quad (K_1 = K_2 = K) \quad (6.14)$$

We shall now take account of the neglected terms. It is easy to see that we have only to replace α^2 , $\alpha c_1 + \alpha c_2$ and $c_1 + c_2$ in (6.11) by $\alpha_1 \alpha_2$, $\alpha_2 c_1 + \alpha_1 c_2$ and $c_1 + c_2 - (K_1 - K_2)^2/M_0^2$, respectively, where

$$\alpha_1 = 1 - (A - K_1/2M_0^2)\chi_{11}, \quad \alpha_2 = 1 - (A - K_2/2M_0^2)\chi_{11}$$

and c_1 and c_2 are now

$$c_1 = 2AK_1 + (K_1/M_0)^2, \quad c_2 = 2AK_2 + (K_2/M_0)^2.$$

We shall write down here only the formula that corresponds to (6.14)

$$\omega/\gamma = [2AK + (K/M_0)^2]^{1/2} \pm H = [(2H_e + H_a)H_a]^{1/2} \pm H, \quad (6.15)$$

where $H_e = AM_0$ and $H_a = K/M_0$. (6.15) was first derived by Kittel (1951).

(b) $H > H_c$. In this case \mathbf{M} is parallel to the x -axis but \mathbf{M}' is perpendicular to it and points parallel to the y -axis. The equations are

$$\begin{aligned} \gamma^{-1} \delta \dot{M}_x &= -(K_2 - K_1)/M_0 \cdot \delta M_z', & \gamma^{-1} \delta \dot{M}_x' &= -2AM_0 \delta M_z, \\ \gamma^{-1} \delta \dot{M}_y &= H \delta M_z, & \gamma^{-1} \delta \dot{M}_y' &= 0, \\ \gamma^{-1} \delta \dot{M}_z &= -H \delta M_y - (K_1/M_0) \delta M_x', & \gamma^{-1} \delta \dot{M}_z' &= 2AM_0 \delta M_x. \end{aligned}$$

These can be separated into two sets, one for δM_x and $\delta M_z'$ and the other for δM_y , δM_z and $\delta M_x'$. (If we did not neglect (6.6), we should not have got such a separation.) The corresponding frequencies are

$$(\omega/\gamma)^2 = c_2 - c_1 \quad (6.16)$$

and

$$(\omega/\gamma)^2 = H^2 - c_1. \quad (6.17)$$

(6.16) corresponds to a mode in which the projections of \mathbf{M}^+ and \mathbf{M}^- on the xy -plane oscillate symmetrically with respect to the x -axis and the vector \mathbf{M}' does a rotational oscillation with the x -axis as the axis of rotation. (6.17) corresponds to a mode in which \mathbf{M}^+ and \mathbf{M}^- are rigidly bound to each other and the vector \mathbf{M} does an elliptic rotation about the x -axis, keeping \mathbf{M}' parallel to the y -axis. The former can be excited by an oscillating magnetic field parallel to the x -axis and the latter by an oscillating field in the yz -plane, particularly one parallel to the z -axis.

6.1.2. The Field is Applied in the xy -plane

This case is fairly complicated because the angle between \mathbf{H} and \mathbf{M}' , that is, ψ , varies with the intensity of the applied field. Yosida (1952) obtained the following equation :

$$\begin{aligned} \left(\frac{\omega}{\gamma}\right)^4 - \left(\frac{\omega}{\gamma}\right)^2 [H^2(\alpha^2 \cos^2 \psi + 1) + c_2 + c_1 \{\cos^2(\psi - \theta_H) - 2 \sin^2(\psi - \theta_H)\}] \\ + H^4 \alpha^2 \cos^2 \psi - H^2 [c_1 \{\alpha \cos^2 \psi \cos 2(\psi - \theta_H) + \alpha \cos \psi \sin \theta_H \sin(\psi - \theta_H) \\ + \sin \psi \cos \theta_H \sin(\psi - \theta_H)\} + c_2 (\alpha \cos^2 \psi - \sin^2 \psi)] + c_1 \cos 2(\psi - \theta_H) \\ \times [c_2 - c_1 \sin^2(\psi - \theta_H)] = 0. \end{aligned} \quad (6.18)$$

In this equation ψ and θ_H are related to each other by (5.12), K being replaced by K_1 .

An approximate form of (6.18) has been obtained by Nagamiya (1951 b) and Keffer and Kittel (1952) neglecting $(H^2/c)^2$ compared with 1 but retaining H^2/c , where $c=c_1=c_2$ because they treated the case of uniaxial anisotropy energy. (The H^4 -terms given in the former's paper are not correct except in the cases of $\theta_H=0$ and $\theta_H=\pi/2$.) Eliminating ψ by (5.12) with $K=K_1$, and retaining terms up to the order of H^4 , we obtain

$$\begin{aligned} \left(\frac{\omega}{\gamma}\right)^4 - \left(\frac{\omega}{\gamma}\right)^2 [c_1 + c_2 + H^2(1 + \alpha^2 \cos^2 \theta_H) - \alpha^2(3 + 2\alpha) c_1^{-1} H^4 \cos^2 \theta_H \sin^2 \theta_H] \\ + c_1 c_2 - H^2 [(c_1 + c_2) \alpha \cos^2 \theta_H - c_2 \sin^2 \theta_H] + H^4 [\alpha^2 + \alpha(2c_2 c_1^{-1} - 1) \\ \times \sin^2 \theta_H] \cos^2 \theta_H = 0. \end{aligned} \quad (6.19)$$

This equation is valid when H is small compared with H_c .

6.1.3. The Field is in the xz -plane

If the field strength is inside the critical hyperbola (5.23), the same equation as (6.18) applies with suffixes 1 and 2 interchanged. On the other hand, if we are outside the critical hyperbola, we obtain after a simple calculation

$$\frac{H_x^2}{c_1 + (\omega/\gamma)^2} - \frac{H_z^2}{(c_2 - c_1) - (\omega/\gamma)^2} = 1. \quad (6.20)$$

6.1.4. The Field is in the yz -plane

This gives

$$\frac{H_y^2}{(\omega/\gamma)^2 - c_1} + \frac{H_z^2}{(\omega/\gamma)^2 - c_2} = 1. \quad (6.21)$$

6.1.5. The Critical Field Resonance

When the field is applied along the x -axis and its strength is just equal to H_c , we have to put $\theta_H=0$ and let ψ be arbitrary in (6.18). The eigenfrequencies vary with the latter angle. If ω_0 is the frequency of the exciting oscillating field, the resonance condition $\omega=\omega_0$ is satisfied at a certain value of ψ for a certain range of the values of the parameters

contained in the frequency equation. We shall not give here the mathematical details, but rather indicate the result by fig. 18, which was obtained by Nagamiya (1954).

Fig. 18

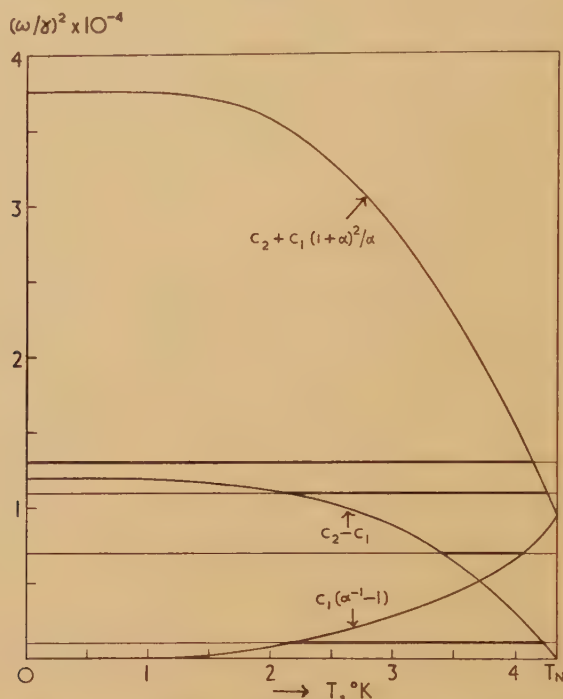


Diagram for obtaining the range of temperature in which resonance takes place at the critical field when the field is applied along the easy axis x . Thick parts of horizontal lines show that range. The heights of these horizontal lines correspond to assumed different values of $(\omega_0'\gamma)^2$, where ω_0 is the applied circular frequency. This diagram is applicable quantitatively to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

6.2. Application to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

Detailed measurements of the antiferromagnetic resonance in this substance have been made by Ubbink (1952, 1953). We shall compare the theoretical results obtained above with his results.

In this substance the g -factor possesses a pronounced anisotropy. Paramagnetic resonance measurements by Itoh, Fujimoto and Ibamoto (1951) at room temperature yielded

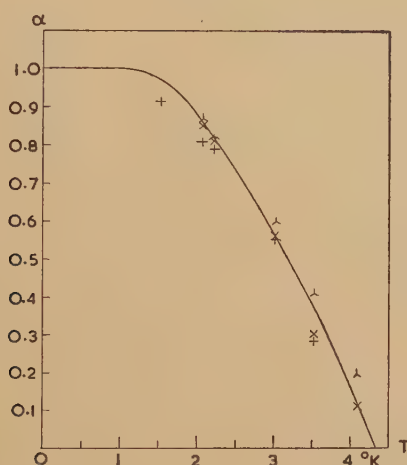
$$g_a = 2.195, \quad g_b = 2.075, \quad g_c = 2.260$$

while susceptibility measurements by van den Handel, Gijsman and Poulis (1952) above the Néel temperature give

$$g_a = 2.20, \quad g_b = 2.03, \quad g_c = 2.24.$$

Applying the argument given at the end of § 4 and making use of the data on the susceptibility below the Néel temperature, given by the latter authors, one obtains a curve for α (fig. 19). Theoretically the ratio c_2/c_1 should be independent of temperature, and its value, determined in the course of comparison between theory and experiment for the resonance absorption, is 3.3. It then remains to determine the parameter c_1 . This can be obtained from the value of the critical field strength along the x -axis ($c_1 = \alpha H_c^2$) for the range in which it is measured by antiferromagnetic resonance, susceptibility and proton resonance measurements. At lower temperatures, where resonance occurs at a field strength different from H_c , formula (6.17) affords its value. Figure 20 gives c_1 as a function of temperature.

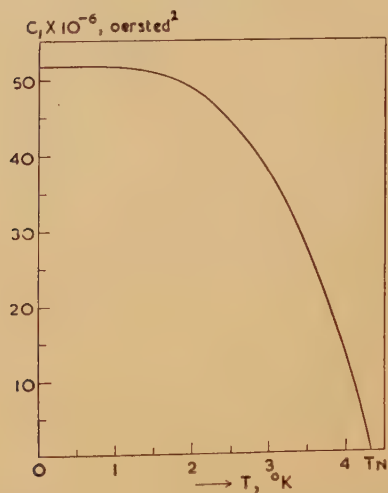
Fig. 19



Curve for $\alpha = 1 - \chi_{II}/\chi_I$ versus temperature for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Experimental points are due to van den Handel, Gijsman and Poulis (1952); \times and $+$ from the susceptibilities χ_{aa} and χ_{ba} with the formula $\alpha = 1 - (g_b/g_a)^2 \chi_{aa}/\chi_{ba}$ with measuring field strength of 3600 oe and 6000 oe, respectively, and λ from χ_{aa} and χ_{ab} with the formula $\alpha = 1 - \chi_{aa}/\chi_{ab}$, where χ_{ba} , for instance, means that the field is applied along the b -axis and the spin direction is along the a -axis.

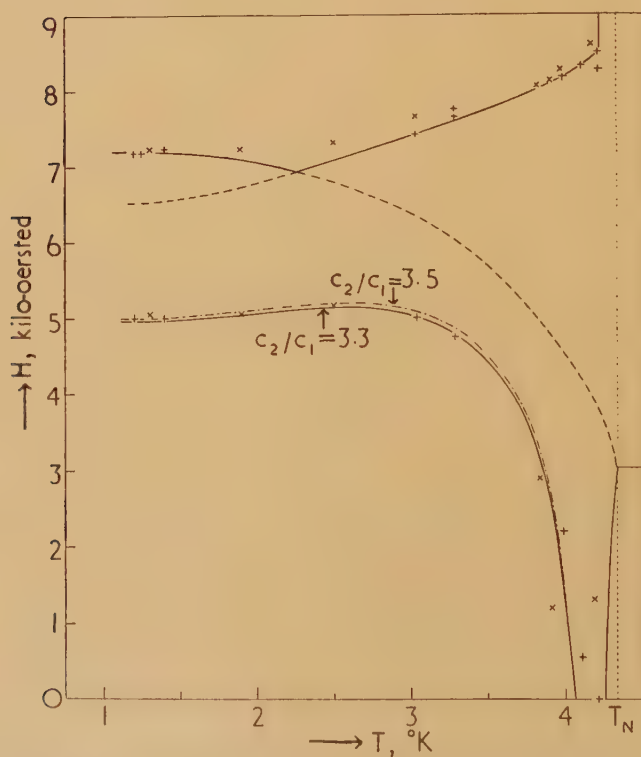
We can now proceed to the comparison between other details of the theory and experiment. Figure 21 shows two resonance values of H as functions of temperature measured by Ubbink with a 3 cm wave. The upper curve has been used to determine the parameters as mentioned above and the lower curve has been calculated by (6.13) with the minus sign for its main part and with the plus sign for the rapidly ascending part near the Néel point. In the upper curve, one should see a kink at 2.25°K , above which temperature resonance takes place along the critical field curve and below which it follows (6.13), but Ubbink's experiment is not accurate enough to confirm the existence of this kink. A remarkable fact that theory predicts and experiment supports is that at 4.225°K

Fig. 20



Curve of c_1 ($=2K_1A$) versus temperature for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

Fig. 21

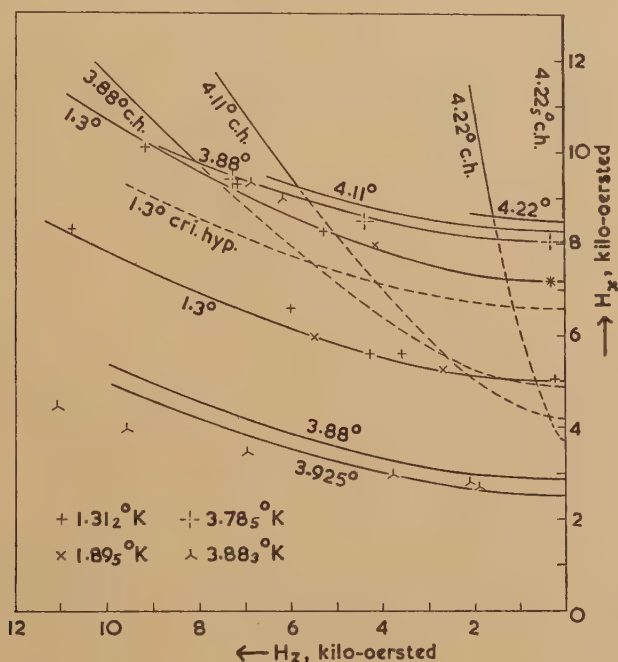


Resonance field strength as functions of temperature when the field is applied along the a -axis; experimental points are after Ubbink (1953 a).

the condition (6.16) is satisfied and that above this temperature resonance along the critical curve vanishes. We therefore have at 4.22_5°K a resonance curve semi-infinitely broad, being cut off for $H < H_c$ and extending indefinitely for $H > H_c$. Such a peculiar curve has actually been observed.

Figure 22 shows the case where the static field is applied in the xz -plane. The curves lying in the lower part have been calculated from (6.18), interchanging the suffixes 1 and 2. In the upper part we have two types of curves. For $T < 2.25^\circ\text{K}$ the critical hyperbola lies lower than the hyperbola given by (6.20), so that resonance takes place along the latter.

Fig. 22



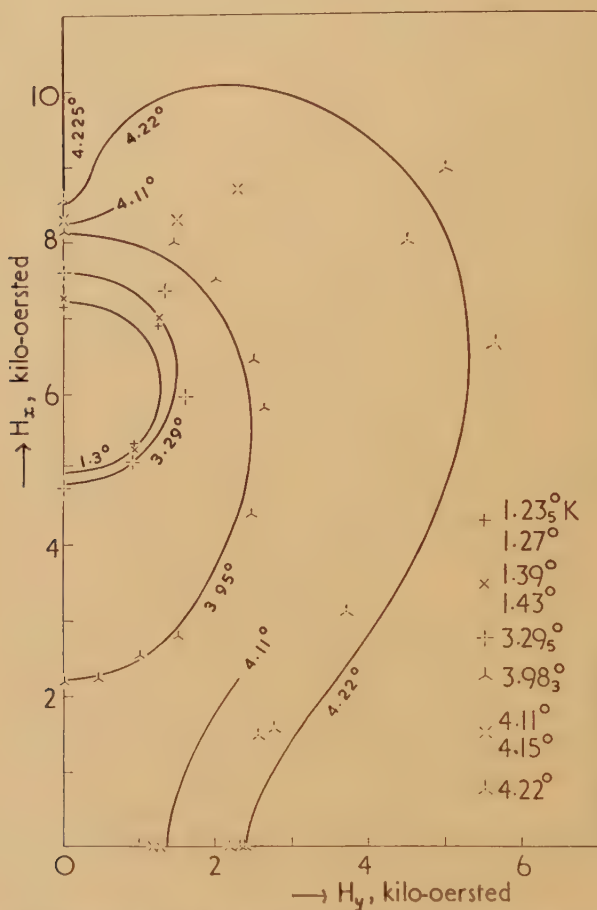
Resonance field curves in the ac -plane; experimental points are after Ubbink (1953 a).

For $T > 2.25^\circ\text{K}$ the situation is reversed near the x -axis, so that resonance takes place at first along the critical hyperbola and then follows (6.20) from the point where these two hyperbolas cross each other. At 4.22_5°K the latter hyperbola degenerates into the x -axis and one then has the situation mentioned above. Figure 23 shows the case where the static field is applied in the xy -plane. All these curves are for a 3 cm wave. We might also mention explicitly that in all these figures the field strengths are actual ones, not H' , although the resonance formulae have been applied with H' in place of H .

6.3. Survey of Theory and Experiment on Antiferromagnetic Resonance

The first experimental work on antiferromagnetic resonance is that due to Trounson, Bleil, Wangsness and Maxwell (1950). They measured the absorption of a microwave of 9300 Mc in Cr_2O_3 and observed that the height of the paramagnetic resonance peak above the Néel point, 47°C , increased when the temperature was lowered towards it. Below the

Fig. 23



Resonance field curves in the ab -plane; experimental points are after Ubbink (1953 a).

Néel point, resonance suddenly vanished and only a broad residual absorption was observed. Maxwell and McGuire (1953) carried out further measurements with a number of antiferromagnetics, including Cr_2O_3 , MnF_2 , MnTe , MnS , MnO and other oxides, and found similar results. In the manganese compounds other than MnF_2 a maximum of the peak height was observed at a certain temperature above the Néel

point, but this temperature practically coincided with T_N in Cr_2O_3 and MnF_2 . The absorption peak broadened as the peak height decreased. They observed even less residual absorption below the Néel point than in the first experiment. The theory of the line broadening was suggested by Tsuya and Ichikawa (1951) and the behaviour of the height of the absorption peak, h , as a function of temperature, above the Néel point was shown by Wangsness (1953 a) to follow the rule

$$h(T) \propto [1 - (\sigma/\sigma_N)][\chi(T)/\chi(T_N)],$$

at least in the case of MnO , where σ is the short-range order parameter and σ_N its value for $T = T_N$.

The theory of antiferromagnetic resonance described in this section was initiated by Kittel (1951) and Nagamiya (1951 b) almost at the same time. Both assumed a uniaxial anisotropy energy and confined themselves to the case of $H < H_c$. Kittel treated the special case of \mathbf{H} parallel to the preferred axis at absolute zero, while Nagamiya gave an equation for the frequency for an arbitrary direction of the applied static field and arbitrary temperature. Keffer and Kittel (1952) obtained the same result as that of Nagamiya and went further on to the case of orthorhombic symmetry. They considered the demagnetizing effect, but this may be of minor importance in common antiferromagnets. The general theory for the case of orthorhombic symmetry, applicable to higher field strengths, is due to Yosida (1952 b) whose analysis appeared almost at the same time as Keffer and Kittel's paper. He missed, however, the resonance at the critical field, which was supplied by Nagamiya (1953, 1954). As seen in the preceding subsection, the Yosida-Nagamiya theory has been successful in describing the experiments on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ done by Ubbink, Poulis, Gerritsen and Gorter (1952, 1953). Ubbink himself explained a part of this experiment by the use of his own theory (Ubbink 1953 a, b, Ubbink, Poulis, Gerritsen and Gorter 1953 and Gorter 1953) for absolute zero and also making use of Yosida's theory. The first report of this stimulating experiment appeared in 1951 (Poulis, van den Handel, Ubbink and Gorter 1951). The most complete account of it is found in Ubbink's thesis (1953 a), which is largely duplicated in a paper in *Physica* (Ubbink, Poulis, Gerritsen and Gorter 1953). The Gorter-Ubbink theory is identical with ours as long as the exchange field is assumed to be much greater than the applied field and anisotropy field. They, however, treated also the case where the applied field is of the order of, or greater than, the exchange field, though they confined their arguments to absolute zero. We have so far not considered this case, but a few remarks will be given in the next section concerning the static problem at such high field strengths.

All these theories predict a strong dependence of the eigen-frequencies upon the direction of the applied field relative to the orientation of the crystal. Therefore, in experiments with powdered samples, we must expect a broad averaged-out pattern of the resonance. One difficulty

encountered at the present time is that the resonance frequencies lie in general in the sub-millimeter region for most antiferromagnetics. An exception is $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, which has a Néel point as low as 4.3°K and consequently the exchange field in it is very small. The resonance thus comes into the ordinary microwave region. There are a few more substances which have a Néel point even lower, but no resonance measurements have yet been made.

The spin-wave theory also gives resonance frequencies at absolute zero for a field applied parallel to the preferred axis (see Part III).

§ 7. TRANSITION FROM ANTIFERROMAGNETIC TO PARAMAGNETIC STATE UNDER A HIGH FIELD

The expression (4.13) for the Néel temperature was derived on the assumption of vanishing external field. For non-vanishing external field one will have non-vanishing sublattice magnetizations and consequently a different value of the Néel temperature. We shall give here the theory of this for three special cases and review the corresponding experiments.

(a) *Field parallel to the preferred axis x and $H < H_c$.*—In this case, \mathbf{M}^+ and \mathbf{M}^- are in line with \mathbf{H} ; \mathbf{M}^- decreases in magnitude with increasing field strength, then becomes parallel to \mathbf{H} (and so to \mathbf{M}^+), and finally coincides with \mathbf{M}^+ . This coincidence occurs continuously, and the corresponding antiferro-paramagnetic transition is of the second kind except when $\Gamma < 0$ and the temperature is sufficiently low (Garrett (1951 b) for $\Gamma \geq 0$, Kanamori, Motizuki and Yosida (1953) for the general case, Sauer and Temperley (1940) for a particular case, and Ziman (1951) for $\Gamma = 0$ with the Ising model and the Bethe approximation). We shall not enter into the mathematical detail of the nature of the transition but will derive the relation between the applied field and the transition temperature. The latter may be called the Néel temperature under an applied field H and will be denoted as $T_N(H)$.

If M^+ , M^- are the algebraic lengths of the vectors \mathbf{M}^+ , \mathbf{M}^- , taken positive when the latter are parallel to \mathbf{H} and negative when antiparallel, we have from (4.7), (4.8) and (4.10)

$$M^+ = M_{00} B_S [(H - A M^- - \Gamma M^+) Sg\mu_B/kT], \text{ etc.}, \quad M_{00} = N Sg\mu_B/2. \quad (7.1)$$

Therefore

$$B_S^{-1}(M^+/M_{00}) - B_S^{-1}(M^-/M_{00}) = (A - \Gamma)(M^+ - M^-) Sg\mu_B/kT,$$

and in the limit of $M^+ \rightarrow M^-$ we have

$$\frac{d}{dM^+} B_S^{-1}(M^+/M_{00}) = (A - \Gamma) Sg\mu_B/kT. \quad \dots (7.2)$$

(7.2), together with (7.1) for $M^+ = M^-$, namely

$$M^+ = M_{00} B_S [(H - (A + \Gamma)M^+) Sg\mu_B/kT] \quad \dots (7.3)$$

determines the Néel temperature as a function of H . An approximate solution can be found by expanding the Brillouin function in powers of its argument, and we obtain, to order H^2 ,

$$[T_N(H) - T_N(0)]/T_N(0) = [3S/(S+1)]^3 B_S'''(0) (8M_{00}^2)^{-1} \chi_1^2 H^2, \quad (7.4)$$

$$B_S'''(0) = -(S+1) [(S+1)^2 + S^2]/90S^3,$$

where $\chi_1 = A^{-1}$ and

$$T_N(0) = C(A - \Gamma)/2. \quad (7.5)$$

For $S=1/2$ the right-hand side of (7.4) is $-(4M_{00}^2)^{-1} \chi_1^2 H^2$. The field corresponding to $T_N(H)=0$ is $H=(A+\Gamma)M_{00}$. Further, we know that the spontaneous magnetization M_0 of each sublattice for $H=0$ obeys the equation

$$M_0 = M_{00} B_S [(A - \Gamma) M_0 S g \mu_B / kT]$$

$$= M_0 T_N(0) / T + \frac{1}{6} M_{00} B_S'''(0) [(A - \Gamma) M_0 S g \mu_B / kT]^3 + \dots,$$

so that (7.4) can be written in another form

$$[T_N(H) - T_N(0)]/T_N(0) = -\frac{3}{4} [(T_N(0) - T)/T M_0^2]_{T \rightarrow T_N(0)} \cdot \chi_1^2 H^2. \quad (7.6)$$

(b) *Field parallel to x but $\mathbf{M}^+ - \mathbf{M}^-$ points along the next preferred axis y ; $H > H_c$.*—In this case the sublattice magnetization vectors \mathbf{M}^+ and \mathbf{M}^- make equal angle with the x -axis and lie in the xy -plane for lower field strengths but they will coincide with the x -axis above a certain high field. This limiting field will be a function of temperature and, conversely, the temperature of this transition will be a function of field strength. Thus we obtain $T_N(H)$.

We assume the effective field acting on \mathbf{M}^+ and \mathbf{M}^- to be given by

$$\mathbf{H}_{\text{eff}}^+ = \mathbf{H} - A \mathbf{M}^- - \Gamma \mathbf{M}^+ + \begin{cases} 0 \\ k_1 M_y^- + k_1' M_y^+ \\ k_2 M_z^- + k_2' M_z^+, \text{ etc.} \end{cases} \quad (7.7)$$

When the applied field is not so strong as to change the magnitudes of \mathbf{M}^+ and \mathbf{M}^- appreciably from their static value M_0 , the coefficients k_1, k_1', k_2, k_2' are connected with the anisotropy constants K_1 and K_2 , defined in § 5, by the following relations :

$$K_1 = (k_1 - k_1') M_0^2, \quad K_2 = (k_2 - k_2') M_0^2. \quad (7.8)$$

The effective field must be parallel to the corresponding sublattice magnetization, so that we put $\lambda \mathbf{M}^+ = \mathbf{H}_{\text{eff}}^+$, etc. Now, if we define \mathbf{M} and \mathbf{M}' as the sum and difference of \mathbf{M}^+ and \mathbf{M}^- , we obviously have only M_x and M_y' as non-vanishing components in the present case, so that the proportionality between \mathbf{M}^+ and $\mathbf{H}_{\text{eff}}^+$, etc. can be written

$$\lambda M_x = 2H - (A + \Gamma) M_x,$$

$$\lambda M_y' = (A - \Gamma - k_1 + k_1') M_y'.$$

If $M_y' \neq 0$; we obtain $\lambda = A - \Gamma - k_1 + k_1'$ and

$$M_x = H / [A - (k_1 - k_1')/2] \quad (7.9)$$

(compare this result with (5.9)), while the magnitude of M^+ is given by

$$M^+ = M_{00} B_S [\lambda M^+ (S g \mu_B / kT)], \quad (7.10)$$

so that M^+ is independent of H . If, on the other hand, $M_y' = 0$, that is $M^+ = M^- = M/2$, M^+ follows the equation (7.3). The transition between these two states gives the Néel temperature as a function of H . That is, $T_N(H)$ can be obtained by eliminating M^+ from (7.9) and (7.10) using the relation $M^+ = M_x/2$. Thus the relation between T_N and H is somewhat similar to that between T and M_0 .

At absolute zero, the value of the critical field is $2[A - (k_1 - k_1')/2] M_0$, which is greater than that of case (a) as long as we assume $\Gamma < A$ (if $\Gamma > A$ the two-sublattice model fails). When the field is not too strong, we obtain the following approximate relation :

$$[T_N(H) - T_N(0)]/T_N(0) = [3S/(S+1)]^3 B_S'''(0) (24M_0^2)^{-1} \chi_1^2 H^2, \quad (7.11)$$

$$T_N(0) = C(A - \Gamma - k_1 + k_1')/2, \quad (7.12)$$

where a simplification is made by putting $\lambda = A - \Gamma$ and $M_x = \chi_1 H$, with $\chi_1 = 1/A$ on the right-hand side of (7.11). The coefficient of H^2 in (7.11) is one third that in (7.4) and the Néel temperature $T_N(0)$, (7.12), is a little lower than (7.5).

(c) *Field is parallel to the y-axis.*—We obtain the same relation as (7.11) but the Néel temperature for zero field is the same as (7.5).

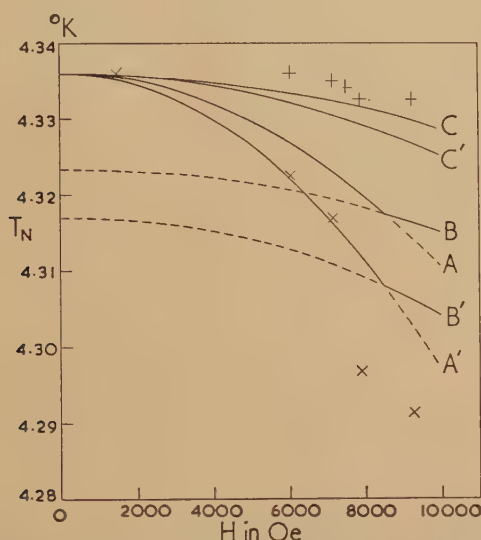
7.1. Comparison with Experiment

Poulis and Hardeman (1952) measured, in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, the change of Néel temperature with applied field, by the method of proton resonance. The field was applied along the a - or b -axis. In fig. 24, parabola A was calculated from (7.6) using experimental values for M_0^2 derived from specific heat measurements (fig. 6); A' was calculated from (7.5), putting $S = 1/2$; B was obtained by taking one third the curvature of A and adjusting its height so as to cross A at the experimental value of H_c at T_N , and B' was obtained in a similar way relative to A'. Parabolas C and C' correspond to the case of a field parallel to the b -axis and were drawn parallel to B and B', respectively. In all these curves a correction for the anisotropy of the g -factor has been made. From the difference of the heights either of A and B or of A' and B' at zero field we can estimate the value of the anisotropy constant K_1 at absolute zero, which is found to be either 0.0044 cm^{-1} per ion or 0.0067 cm^{-1} per ion, respectively; the value estimated from antiferromagnetic resonance (see § 6 and § 10) is 0.0051 cm^{-1} per ion, which is thus in good agreement.

Garrett (1951 a) made adiabatic measurements of a number of characteristic quantities of $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ whose Néel point is 0.084°K and in which the exchange field is of the order of 400 oe. He derived two sets of curves representing $M = \text{constant}$ and $\text{entropy} = \text{constant}$ in the T - H -plane and obtained from them a curve that separates the antiferromagnetic region from the paramagnetic region, that is, the relation between T_N and H . The field was applied along the preferred axis, so that we have to distinguish two cases a and b . In the first case we have, theoretically, increasing M/H for constant H as a function of T in the antiferromagnetic

region, with a maximum at the Néel point, whereas in the second case we have a constant value of M/H up to the Néel temperature and a decreasing value above. Garrett's experiments appear to favour the first case, so that it seems that the spins cannot deviate from the preferred axis in the antiferromagnetic state even at a field comparable to the exchange field; the crystalline field acting on each atomic magnetic moment appears to be too strong. In such a case, one would naturally have to incorporate the crystalline field into the effective field from the very beginning, but one would then obtain a function similar to the Brillouin function in its general behaviour, if the molecular field type of approximation is made.

Fig. 24



Decrease of the Néel temperature with applied field strength for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.
 + represent the observed values when the field is applied along the b -axis and \times represent those when the field is applied along the a -axis (Poulis and Hardeman 1952). Curves A, B, C and A', B', C' are explained in the text.

Henry (1953, 1954) measured the isothermal magnetizations of spherical samples of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, at liquid helium temperatures as functions of applied field strength, up to 58 000 oe. He confirmed that the relation (7.3) holds very well with $S=5/2$, where $2M^+$ is the magnitude of the magnetization, and obtained at saturation

$$(A + I')M_{00} = 14\,000 \text{ oe for } \text{MnCl}_2 \cdot 4\text{H}_2\text{O}, \quad 18\,000 \text{ oe for } \text{MnBr}_2 \cdot 4\text{H}_2\text{O}.$$

He also measured the magnetization, at constant field strength, as a function of temperature, and observed a maximum at a temperature, T_{max} , which varied with the field strength H , though the lower limit of temperature in his experiment was 1.3°K and the corresponding highest value of H for which the maximum was observed was in the neighbourhood

of 20 000 oe. If this T_{\max} could be identified with $T_N(H)$, his result should be explained by a theory of the type described above. Unfortunately, the anisotropy energy is not known in these substances and, moreover, the simple theory above does not apply to polycrystalline specimens. Nevertheless, if we assume the anisotropy energy to be negligible in his experiments and apply the case b , putting $k_1=k_1'=0$, the general features of his results appear to conform to the theory. The T_N - H curve begins with a parabolic shape at lower field strengths and appears to end at a field strength of the order of $(A+\Gamma)M_{00}$, given above. The theoretical value for the terminal field strength is $2AM_{00}$ and should thus be greater than that observed (but, at most, twice as large, so long as we assume $A>\Gamma$). Quantitative comparison cannot be made since the value of χ_1 is not known. By extrapolating $T_N(H)$ to $H=0$, one obtains

$$T_N(0)=1.67^\circ\text{K for the chloride, } 2.2^\circ\text{K for the bromide.}$$

The former is in good agreement with the value obtained from specific heat measurements by Friedberg and Wasscher (1953), which yielded 1.622°K .

PART II. INDIRECT EXCHANGE INTERACTION AND ANISOTROPY ENERGY

§ 8. SUPEREXCHANGE AND DOUBLE EXCHANGE INTERACTIONS

8.1. *Theory of Kramers, Anderson and van Vleck*

The majority of the substances which show antiferromagnetic properties are ionic crystals such as MnO , MnS , MnF_2 , etc. In these substances the magnetic ions are separated from each other by the anions O, S, F, etc. Neutron diffraction studies on MnO , FeO , CoO and NiO , by Shull and others (1951), revealed that there exists a strong antiferromagnetic exchange coupling between next-to-nearest magnetic ions, which are separated by the intervening large oxygen ions. The Néel temperature, which is a measure of the strength of this exchange coupling, is 122°K for MnO , for instance, which is not much lower than the Curie temperatures of ordinary ferromagnetic substances. This fact indicates that the antiferromagnetic coupling in such substances arises from a mechanism definitely different from that of the usual direct exchange interaction.

The existence of such an indirect exchange interaction is also found in magnetically diluted salts, such as Tutton salts and alums. The analysis of the experimental data for the paramagnetic susceptibility and specific heat at low temperatures of these substances confirms the existence of an exchange coupling between magnetic ions separated from each other by a distance as large as $5\sim 10$ Å. For instance, the paramagnetic Curie temperature, deduced from the temperature dependence of the susceptibility, is 0.7°K for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in which the nearest distance between magnetic ions amounts to 5.55 Å.

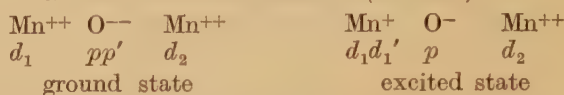
The mechanism of superexchange, different from the direct exchange familiar since Heisenberg's original theory of ferromagnetism, was proposed by Kramers as early as 1934 to explain the magnetic behaviour of such paramagnetic salts. His treatment was based on a perturbation calculation. Then, Bizette (1946) and Néel (1948) emphasized the importance of this superexchange in antiferromagnetic substances, and Anderson (1950 a) presented a detailed theoretical treatment of Kramers' idea and clarified the mechanism of superexchange. The same problem was treated by van Vleck (1951) using a different method.

Anderson isolates one oxygen ion and the two adjacent magnetic ions as shown in fig. 25, and considers, for simplicity, two electrons occupying the same p -orbital of the O^{--} ion and one electron each in a d -orbital of the magnetic ions. In this state the two electrons in O^{--} will form a singlet state, so that there will be no exchange coupling between magnetic ions M_1 and M_2 . One can think, however, of the possibility of one of the two electrons of the O^{--} ion being transferred to one of the two magnetic ions, say M_1 , and occupying its s - or d -orbital. In this excited state, the unpaired electron left in O^{--} can couple with the electron of

the other magnetic ion M_2 . There should also be a strong coupling between the electron transferred to M_1 and the original electron in M_1 . Moreover, the two electrons originally belonging to the oxygen ion have opposite spins, so that there will appear an indirect spin coupling between M_1 and M_2 through this excited state. In this way, Anderson could explain the superexchange coupling between magnetic ions separated by a non-magnetic ion.

Fig. 25

Ground and excited states of $(\text{MnOMn})^{++}$.



The mathematical details of this superexchange mechanism are given in the original articles of Anderson and van Vleck and we might not, perhaps, need to reproduce them here. However, we wish to go a little further, and for our purpose it is convenient to give here a short account of the mathematical method.

Let us denote the ground configuration by A and the excited configuration by B . Then configurations A and B are represented by the following wave functions :

$$A : \psi_{d1}(1) \psi_p(2) \psi_p(3) \psi_{d2}(4), \quad . \quad . \quad . \quad . \quad . \quad (8.1a)$$

$$B : \psi_{d1}(1) \psi_{d1'}(2) \psi_p(3) \psi_{d2}(4). \quad . \quad . \quad . \quad . \quad . \quad (8.1b)$$

The perturbing Hamiltonian of this four-electron system can be considered, for convenience, to consist of the following two parts :

$$V = V_t + V_e, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

where V_t represents that part of the perturbation which connects the ground configuration A to the excited configuration B and is, for simplicity, assumed to be spin-independent, and V_e represents the spin-dependent part, which is assumed to be diagonal with respect to the orbital states.

As mentioned before, the p -orbital of the O^{--} ion is occupied by paired electrons in the ground state and so there is no spin coupling between the O^{--} ion and its adjacent magnetic ions. Accordingly the first order perturbation energy vanishes. The second order energy does not depend upon the spin configurations on account of the assumption just made concerning V_t and V_e . According to the ordinary perturbation theory the third order energy is given by

$$E_3 = \sum_{i,r} \sum_{j,s} \frac{(g, t | V | i, r)(i, r | V | j, s)(j, s | V | g, u)}{(E_{i,r} - E_{g,t})(E_{j,s} - E_{g,u})} - \sum_{i,r} \frac{(g, t | V | i, r)(i, r | V | g, t)(g, t | V | g, t)}{(E_{i,r} - E_{g,t})^2}, \quad . \quad . \quad (8.3)$$

where g and i, j denote the ground state and the excited states, respectively, and r, s, t and u denote spin configurations. Applying this formula to

our case of two configurations, we obtain the following non-vanishing term :

$$E_3 = \sum_{t', u'} \frac{(A^t | V_t | B^{t'})(B^{t'} | V_e | B^{u'})(B^{u'} | V_t | A^u)}{(E_B^{t'} - E_A^t)(E_B^{u'} - E_A^u)}, \quad . \quad . \quad (8.4)$$

where again t and u denote spin configurations.

In his original paper Anderson used Serber's method of the Dirac vector model, extended so as to include different configurations. Here we shall, however, follow a more straightforward procedure employed by van Vleck. First, with van Vleck, we shall regard the two orbitals of O^{--} as different and denote them by p and p' . We denote by $\psi^3 [(d_1 d_2)^3 (pp')^1]$ the wave function of the triplet state for the four-electron system in which the spins of the two electrons occupying the d_1 -orbital of M_1 and the d_2 -orbital of M_2 are parallel and those of the electrons occupying the p and p' -orbitals of O^{--} are antiparallel. Similar notation will be used for other states. If we recombine $(d_1 d_2) (pp')$ in such a for as $(pd_1) (p'd_2)$, we find

$$\begin{aligned} \psi_A^1 [(pp')^1 (d_1 d_2)^1] &= \sqrt{\frac{3}{4}} \psi_A^1 [(pd_1)^3 (p'd_2)^3] + \frac{1}{2} \psi_A^1 [(pd_1)^1 (p'd_2)^1], \\ \psi_A^3 [(pp')^1 (d_1 d_2)^3] &= \frac{1}{2} \{ \psi_A^3 [(pd_1)^1 (p'd_2)^3] + \psi_A^3 [(pd_1)^3 (p'd_2)^1] \} \\ &\quad + \sqrt{\frac{1}{2}} \psi_A^3 [(pd_1)^3 (p'd_2)^3]. \quad . \quad . \quad . \quad . \quad . \quad (8.5) \end{aligned}$$

These relations can be proved by comparing spin functions for the two systems. For instance, the spin function of $\psi_A^1 [(pp')^1 (d_1 d_2)^1]$ is represented by

$$\frac{1}{2} \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \} \{ \alpha(3)\beta(4) - \alpha(4)\beta(3) \},$$

where it is assumed that electrons 1 and 2 occupy the orbitals p and p' and electrons 3 and 4 the orbitals d_1 and d_2 . This can be written in another form

$$\begin{aligned} &\sqrt{\frac{3}{4}} [(1/\sqrt{2}) \{ \alpha(1)\beta(4) + \alpha(4)\beta(1) \} \{ \alpha(2)\beta(3) + \alpha(3)\beta(2) \} \\ &\quad - 2 \{ \beta(1)\beta(4)\alpha(2)\alpha(3) + \alpha(1)\alpha(4)\beta(2)\beta(3) \}] \\ &\quad + \frac{1}{2} [(1/\sqrt{4}) \{ \alpha(1)\beta(4) - \alpha(4)\beta(1) \} \{ \beta(2)\alpha(3) - \alpha(2)\beta(3) \}]. \end{aligned}$$

In this expression the portion enclosed in heavy brackets in the first term represents the spin function of $\psi_A^1 [(pd_1)^3 (p'd_2)^3]$ and that in the second term the spin function of $\psi_A^1 [(pd_1)^1 (p'd_2)^1]$.

Spin configurations for the excited state can be represented by

$$\begin{aligned} \psi_{B_a}^{1,3} [(d_1 d_1')^3 (pd_2)^3], \quad \psi_{B_b}^1 [(d_1 d_1')^1 (pd_2)^1], \\ \psi_{B_c}^3 [(d_1 d_1')^1 (pd_2)^3], \quad \psi_{B_d}^3 [(d_1 d_1')^3 (pd_2)^1], \quad . \quad . \quad (8.6) \end{aligned}$$

where d_1' is the orbital of M_1 to which an electron has been transferred from O^{--} .

In the excited state, V_e can be expressed as

$$V_e = -\frac{1}{2} J_{pd} (1 + 4 (\mathbf{s}_1 \cdot \mathbf{s}_2)). \quad . \quad . \quad . \quad (8.7)$$

Then, by use of (8.5), (8.6) and (8.7), we can calculate the matrix elements included in (8.4). The results are as follows :

$$\left. \begin{aligned} (A^1 | V_t | B_a^1) &= -\sqrt{\frac{3}{4}} \cdot b, & (A^1 | V_t | B_b^1) &= \frac{1}{2} b, \\ (A^3 | V_t | B_a^3) &= -\sqrt{\frac{1}{2}} \cdot b, & (A^3 | V_t | B_c^3) &= \frac{1}{2} b, \\ (A^3 | V_t | B_d^3) &= -\frac{1}{2} b, \\ (B_a^{1,3} | V_e | B_a^{1,3}) &= (B_c^3 | V_e | B_c^3) = -J_{pd}, \\ (B_b^1 | V_e | B_b^1) &= (B_d^3 | V_e | B_d^3) = +J_{pd}, \end{aligned} \right\} \quad \text{. . . (8.8)}$$

where b represents the transfer integral

$$b = \int \psi_{d_1}(1) V_t \psi_p(1) d\tau_1 \quad \text{. (8.10)}$$

and J_{pd} the exchange integral between the p -orbital of the O^{--} and the d -orbital of the magnetic ion,

$$J_{pd} = \int \psi_p(1) \psi_d(2) V_e \psi_p(2) \psi_d(1) d\tau_1 d\tau_2 \quad \text{. (8.11)}$$

We insert (8.8) and (8.9) into (8.4) and observe that

$$E_{B_a^{1,3}} = E_{B_d^3} = \Delta E(t) \quad \text{and} \quad E_{B_b^1} = E_{B_c^3} = \Delta E(s), \quad \text{. (8.12)}$$

where $\Delta E(t)$ and $\Delta E(s)$ represent respectively the energy of the triplet and singlet states of the metallic ion which has received an extra electron from O^{--} in the excited configuration, thus we finally obtain

$$\begin{aligned} E(\text{triplet}) &= \frac{1}{2} \{ 1/\Delta E(t)^2 - 1/\Delta E(s)^2 \} \frac{1}{4} b^2 J_{pd} - \frac{1}{8} \{ 3/\Delta E(t)^2 + 1/\Delta E(s)^2 \} b^2 J_{pd}, \\ E(\text{singlet}) &= \frac{1}{2} \{ 1/\Delta E(t)^2 - 1/\Delta E(s)^2 \} \{ -\frac{3}{4} b^2 J_{pd} \} \\ &\quad - \frac{1}{8} \{ 3/\Delta E(t)^2 + 1/\Delta E(s)^2 \} b^2 J_{pd}. \end{aligned}$$

These two equations can be expressed as a single equation, as follows :

$$E = \frac{1}{2} (1/\Delta E(t)^2 - 1/\Delta E(s)^2) b^2 J_{pd} (\mathbf{s}_{d_1} \cdot \mathbf{s}_{d_2}) - \frac{1}{8} (3/\Delta E(t)^2 + 1/\Delta E(s)^2) b^2 J_{pd} \quad \text{. (8.13)}$$

In deriving (8.13), it was assumed that the two p -orbitals of O^{--} were different from each other and also that only one of the metallic ions could receive an extra electron. Since, actually, either metallic ion can receive the electron, with equal probability, the right-hand side of (8.13) must be doubled. Anderson has shown that for a pair of identical p -orbitals the transfer integral b must be multiplied by $\sqrt{2}$, except when d_1 and d_1' are also identical, in which case this is not necessary. The other assumption used in deriving (8.13) is that all the orbitals are orthogonal to each other except for the expression of the exchange integral J_{pd} , which can be negative for non-orthogonal orbitals. Anderson has also generalized his calculation to the case of spin S greater than $\frac{1}{2}$ and shown that an expression of the form of (8.13) does still hold.

If, in the excited configuration, the parallel spin state is excluded by the Pauli principle, we must put $\Delta E(t) = \infty$ in (8.13). Then we see that M_1 and M_2 are coupled by an exchange integral which has the same sign as J_{pd} . If, on the other hand, the antiparallel spin state is excluded by a strong Hund's rule effect, we must put $\Delta E(s) = \infty$. Then we see that the effective exchange integral has the sign opposite to that of J_{pd} .

From the above calculation it may be concluded that there exists a coupling of the form $J(\mathbf{s}_1 \cdot \mathbf{s}_2)$ between the spins of the two magnetic ions and that the order of magnitude of the effective exchange integral J is proportional to the product of the direct exchange integral J_{pd} with the square of the transfer integral b^2 . We also see that the superexchange has a directional property corresponding to that of the p -orbital. The p -orbital of the O^{--} ion which extends towards both magnetic ions will have a large overlap with them. We expect, therefore, a strong superexchange coupling between those magnetic ions which are situated oppositely with respect to the oxygen ion. This directionality explains the fact that a strong exchange coupling exists between next-to-nearest Mn ions in MnO .

There is a considerable overlap between the magnetic ions and the oxygen ion, so that it is reasonable to suppose the direct exchange integral J_{pd} to be negative. If the magnetic ion has a more-than-half-filled shell, the transferred electron will set its spin antiparallel to that of the magnetic ion on account of the Pauli principle, while, if the magnetic ion has a less-than-half-filled shell, the electron's spin will become parallel on account of a strong Hund rule effect. We expect, therefore, an antiferromagnetic coupling between magnetic ions in the former case and a ferromagnetic coupling in the latter case. In fact, it has been experimentally recognized that oxides, sulphides and fluorides of Ni^{2+} , Co^{2+} , Fe^{2+} and Mn^{2+} show antiferromagnetism. It is a remarkable fact that $MnTe$ exhibits antiferromagnetism and $CrTe$ ferromagnetism. It has been pointed out by Shimizu (1952), however, that some compounds of magnetic ions with a less-than-half-filled shell are antiferromagnetic, contrary to the prediction (see table 1). Shimizu has emphasized that, if the Hund rule does not operate so strongly as to exclude antiparallel configurations, we can not omit the $\Delta E(s)^2$ -dependent term in (8.13) and also that, when the many electrons belonging to one Mn ion are taken into account, there are other contributions arising from configurations not considered above. Even after taking these into consideration, one will see that the dominant term comes from the Hund rule effect. There are two possible ways for the antiferromagnetic terms to overcome the ferromagnetic ones. The first is that the large number of antiparallel configurations may compensate for their energies being higher than those of parallel configurations. This possibility was suggested by Anderson. The other possibility, which is due to Polder (1951), is that the crystalline field may lower the energy of the antiparallel configurations.

8.2. Other Superexchange Effects

Slater (1953) has proposed, as another mechanism of superexchange, that the polarization or deformation of the oxygen ion stabilizes the energy of the antiferromagnetic state of $Mn-O-Mn$. According to his idea, the potential energy of an electron with plus spin is, on account of the exchange effect or Hund's rule effect, effectively lower when it stays in the charge

distribution of other electrons with plus spins than when it stays in the charge distribution of electrons with minus spins, if the distributions are the same. Therefore, when we have an antiferromagnetic configuration of Mn-O-Mn, in which the spins of one Mn ion point in one direction and those of the other Mn ion in the opposite direction, the electrons of the oxygen ion with plus and minus spins will be pulled each towards that Mn ion which has the same spin direction. In this way the oxygen ion is polarized and the antiferromagnetic state is stabilized. This effect does not occur in the ferromagnetic state. Similar effects of polarization can occur if there is a covalent bonding, where, however, electrons of plus spin are attracted by the Mn of minus spin and those of minus spin by the Mn of plus spin.

Pratt (1953), following Slater's idea, has calculated in detail the energies of ferromagnetic and antiferromagnetic states of $(\text{Mn-O-Mn})^{2+}$, using orthogonalized orbitals. He took into account the same excited configuration as that considered by Anderson and van Vleck. However, he obtained the unreasonable result that the ferromagnetic state should be more stable than the antiferromagnetic one. When he used non-orthogonal orbitals, somewhat simplifying the model, this result was improved. Yamashita (1954) has also discussed the effect of the non-orthogonality of the orbitals of Mn and O ions, in the Heitler-London-Löwdin approximation.

Slater and Pratt's mechanism of superexchange is a little different from Anderson's in that they included in the excited configurations a simultaneous transfer of the oxygen electrons to the right and left Mn ions.

Anderson and Hasegawa (1954) have found another superexchange which arises from the same mechanism as that proposed by Slater. This acts antiferromagnetically in both of the cases of more-than and less-than-half-filled shells. The effect comes from the term

$$E = \sum_{u, u'} \frac{(A^t | V_t | B_1^u)(B_1^u | V_c | B_2^{u'})(B_2^{u'} | V_t | A^t)}{(E_{B_1^u} - E_{A^t})(E_{B_2^{u'}} - E_{A^t})} \quad (8.14)$$

which has been ignored in (8.4). Here $(B_1^u | V_c | B_2^{u'})$ means the matrix element of V_c between the excited state in which the right Mn ion has an excess electron and that in which the left Mn ion has an excess electron. The excited wave functions of B_2 are given by replacing d_1 and d_1' in (8.6) by d_2 and d_2' , and are as follows :

$$\left. \begin{aligned} \psi_{B_{2a}}^{1,3} [(d_2 d_2')^3 (p d_1)^3], & \quad \psi_{B_{2b}}^1 [(d_2 d_2')^1 (p d_1)^1], \\ \psi_{B_{2c}}^3 [(d_2 d_2')^3 (p d_1)^1], & \quad \psi_{B_{2d}}^3 [(d_2 d_2')^1 (p d_1)^3]. \end{aligned} \right\} \quad (8.15)$$

Here the suffixes c and d are interchanged for convenience. Then, the non-vanishing matrix elements of $(B_1^u | V_e | B_2^{u'})$ are

$$\left. \begin{aligned} (B_{1a}^{1,3} | V_e | B_{2a}^{1,3}) &= +J^*, & (B_{1b}^1 | V_e | B_{2b}^1) &= +J^*, \\ (B_{1c}^3 | V_e | B_{2c}^3) &= -J^*, & (B_{1d}^3 | V_e | B_{2d}^3) &= -J^*, \end{aligned} \right\} \quad (8.16)$$

where J^* means the integral

$$J^* = \int \psi_{d_1}(1) \psi_p(1) V_e \psi_p(2) \psi_{d_2}(2) d\tau_1 d\tau_2. \quad (8.17)$$

Noticing that the transfer integrals for B_2 are equal to those for B_1 , (8.8), except for the sign, namely,

$$\left. \begin{aligned} (A^1 | V_t | B_{2a}^1) &= \sqrt{\frac{3}{4}} \cdot b, & (A^1 | V_t | B_{2b}^1) &= -\frac{1}{2}b, \\ (A^3 | V_t | B_{2a}^3) &= \sqrt{\frac{1}{2}} \cdot b, \\ (A^3 | V_t | B_{2c}^3) &= \frac{1}{2}b, & (A^3 | V_t | B_{2d}^3) &= -\frac{1}{2}b, \end{aligned} \right\} \quad (8.18)$$

we obtain the following results :

$$\left. \begin{aligned} E(\text{triplet}) &= -\{1/\Delta E(t)^2 + 1/\Delta E(s)\} \frac{1}{2}b^2J^*, \\ E(\text{singlet}) &= -\{3/\Delta E(t)^2 + 1/\Delta E(s)\} \frac{1}{4}b^2J^*. \end{aligned} \right\} \quad (8.19)$$

These equations are equivalent to

$$\begin{aligned} E &= \frac{1}{4}b^2J^* \{1/\Delta E(t) - 1/\Delta E(s)\}^2 (\mathbf{s}_{d_1} \cdot \mathbf{s}_{d_2}) \\ &\quad - (1/16)b^2J^* \{3/\Delta E(t) + 1/\Delta E(s)\}^2. \end{aligned} \quad (8.20)$$

(8.20) shows that the sign of the effective exchange integral is always equal to that of J^* irrespective of whether $3d$ shell is more-than or less-than-half-full. The integral J^* may be approximated by $2S_{pd_2}b$, where S_{pd_2} is the overlap integral between d_2 and p -orbitals. On the other hand, the ordinary exchange integral J_{pd} is of the order of $2S_{pd_1}b$. Since S_{pd_1} has a sign opposite to that of S_{pd_2} , we see that J^* and J_{pd} are equal in magnitude but opposite in sign and that the term furnished by (8.20) operates always antiferromagnetically.

The inclusion of this term would make Anderson's original treatment come nearer to Slater's effect of polarization. We might add, however, that there is also an effect of polarization arising from the excited configuration in which an electron of the oxygen ion is excited to its $3s$ state. Pratt (1953) also calculated this effect, basing his calculation on a simple model, and showed that it is less important than that arising from the excited states considered above.

8.3. Double Exchange

Zener (1951) proposed another kind of indirect spin-spin interaction to account for the ferromagnetic properties found in mixed crystals of LaMnO_3 and BaMnO_3 (or other alkaline earth manganites), neither of which is known to show ferromagnetism in itself. These mixed crystals include Mn^{3+} and Mn^{4+} ions, and Zener considered that an indirect spin-spin interaction works between Mn^{3+} and Mn^{4+} by the following mechanism. Consider for simplicity one oxygen ion and its adjacent two Mn ions. In order to simplify the model we focus our attention, as before, on the two paired electrons of O^{2-} , and assume that one of these two Mn ions has one electron and that the other has two electrons with spins parallel owing to a strong Hund rule effect. We shall call the state in which the two Mn ions have parallel spins configuration I.

This can change into configuration II, shown in fig. 26, by the transfer of an electron of that spin direction from O^{2-} to the right Mn (which had been occupied by one electron). Further, the configuration II can change into another configuration III by the transfer of one of the electrons of the left Mn to the vacant orbital of O^{2-} produced by the first transfer.

Fig. 26

Ground and excited configurations of $(MnOMn)^{5+}$.

Mn^{3+}	O^{2-}	Mn^{4+}	Mn^{3+}	O^{-}	Mn^{3+}	Mn^{4+}	O^{2-}	Mn^{3+}
$d_1 d_1'$	pp'	d_2	$d_1 d_1'$	p	$d_2 d_2'$	d_1	pp'	$d_2 d_2'$
configuration I			configuration II			configuration III		

Configuration I has the same energy as that of configuration III, and therefore a strong resonance will take place between them through the excited configuration II. Thus the ferromagnetic state will be stabilized. For two Mn ions with antiparallel spins, such a resonance is not expected. Therefore, a ferromagnetic spin coupling appears between Mn^{3+} and Mn^{4+} . Zener called this type of coupling the 'double exchange'.

Anderson (1954) calculated the energy splitting due to this double exchange. Each of the configurations I and III has one quartet and two doublets whose wave functions can be written, in the notation employed in §§ 8.1 and 8.2, as

$$\left. \begin{aligned} \psi_{I_a}^{4,2} [(d_1 d_1')^3 (d_2)], & \quad \psi_{I_b}^2 [(d_1 d_1')^1 (d_2)], \\ \psi_{III_a}^{4,2} [(d_1)(d_2 d_2')^3], & \quad \psi_{III_b}^2 [(d_1)(d_2 d_2')^1]. \end{aligned} \right\} \quad (8.21)$$

As in the case of superexchange, we have the following relations between two systems $(d_1 d_1')(d_2)$ and $(d_1)(d_2 d_1')$:

$$\left. \begin{aligned} \psi^4 [(d_1 d_1')^3 (d_2)] &= \psi^4 [(d_1)(d_2 d_1')^3], \\ \psi^2 [(d_1 d_1')^3 (d_2)] &= \sqrt{\frac{3}{4}} \psi^2 [(d_1)(d_2 d_1')^1] - \frac{1}{2} \psi^2 [(d_1)(d_2 d_1')^3], \\ \psi^2 [(d_1 d_1')^1 (d_2)] &= \frac{1}{2} \psi^2 [(d_1)(d_2 d_1')^1] + \sqrt{\frac{3}{4}} \psi^2 [(d_1)(d_2 d_1')^3]. \end{aligned} \right\} \quad (8.22)$$

We assume again that the effective Hamiltonian, $\mathcal{H}_{I,III}$, giving rise to the transfer is spin-independent; then the non-vanishing matrix elements of $\mathcal{H}_{I,III}$ can easily be calculated by use of (8.22), i.e.

$$\left. \begin{aligned} (I_a^4 | \mathcal{H}_{I,III} | III_a^4) &= b, & (I_a^2 | \mathcal{H}_{I,III} | III_a^2) &= -\frac{1}{2}b, \\ (I_a^2 | \mathcal{H}_{I,III} | III_b^2) &= \sqrt{\frac{3}{4}}b, & (I_b^2 | \mathcal{H}_{I,III} | III_a^2) &= \sqrt{\frac{3}{4}}b, \\ (I_b^2 | \mathcal{H}_{I,III} | III_b^2) &= \frac{1}{2}b. \end{aligned} \right\} \quad (8.23)$$

Thus, the degeneracy of the configurations I and III is entirely removed by the transfer Hamiltonian $\mathcal{H}_{I,III}$. Denoting by $\Delta E(t)$ and $\Delta E(s)$ the energies of the states in which two electrons on the same Mn have spins parallel and antiparallel, respectively, we obtain energy eigenvalues for the quartet state

$$E_q = \Delta E(t) \pm b \text{ (quartet)} \quad (8.24a)$$

and for the doublets, assuming the strong Hund rule,

$$E_{d_1} = \Delta E(t) \pm \frac{1}{2}b \quad \text{and} \quad E_{d_2} = \Delta E(s) \text{ (doublets)}. \quad (8.24b)$$

From these results, we may conclude that double exchange shows rather strange properties, very different from those of superexchange; thus, double exchange interaction cannot be expressed in the convenient form of a multiple of $(\mathbf{s}_1 \cdot \mathbf{s}_2)$ and the average energy value of the state of higher multiplicity (quartet) is equal to that of one of the states of lower multiplicity (doublets). Anderson suggests that one cannot therefore expect the Curie-Weiss law to hold for the susceptibility of substances which involve double exchange and also that, in them, the approximation of the Weiss molecular field cannot be justified.

The double exchange is intimately connected with electron transfers and accordingly with electric conductivity. Zener has shown that the resonance energy b is proportional to the diffusion coefficient of the Mn^{4+} ions and thus explained qualitatively the relation between the magnetic behaviour and the conductivity observed in manganites.

§ 9. ORIGIN OF THE ANISOTROPY ENERGY

9.1. *Three Sources of the Anisotropy Energy; Anisotropy Energy due to Crystalline Electric Field*

In § 6 we introduced anisotropy energy in a phenomenological way. We shall now investigate the atomic origin of the anisotropy energy. The ordinary exchange energy and superexchange energy, which have the form of the scalar product of two spins \mathbf{S}_1 and \mathbf{S}_2 , do not give rise to anisotropy energy. Two kinds of anisotropic interactions can be considered: one is the dipolar interaction between magnetic moments and the other is a somewhat complicated one, called usually 'anisotropic exchange interaction' or 'pseudo-dipolar interaction'. The latter is a combined effect of \mathbf{LS} coupling and exchange interaction. This interaction was proposed by van Vleck (1937 b, 1951) and is particularly important in ferromagnetic metals. Beside these two anisotropic interactions, the crystalline field acting on each magnetic ion produces an anisotropy energy, expressible as a function of the spin of the magnetic ion. The anisotropy of the g -factor usually found in paramagnetic salts originates also in the anisotropy of the crystalline field. Thus, the anisotropy energy in antiferromagnetic substances can be considered to stem from three sources: magnetic dipolar interaction, anisotropic exchange interaction and the anisotropy of the crystalline field. However, the effects of these three parts are quite different in different substances. They also give rise to the anisotropy of the susceptibility above the Néel temperature, just as in paramagnetic substances.

When a free magnetic ion is brought into the crystalline electric field arising from the surrounding plus and minus ions, the directional degeneracy of the orbital angular momentum is removed, completely or partially, because of the crystalline Stark effect. For simplicity we shall here assume that the ground state is not degenerate, namely, that in this state the orbital angular momentum is completely quenched.

Then we can suppose that the magnetic moment possessed by a magnetic ion in the ground state is the spin magnetic moment only, namely, $2\mu_B \mathbf{S}$ where μ_B is the Bohr magneton and \mathbf{S} denotes the spin angular momentum vector measured in units of \hbar . However, since the off-diagonal elements of the angular momentum \mathbf{L} (measured in units of \hbar) between the ground state and the excited states are finite, even if the average value of \mathbf{L} vanishes in the ground state, the orbital moment is also capable of contributing to the magnetic moment in the second order perturbation, if one takes the \mathbf{LS} coupling and the Zeeman energy as perturbing Hamiltonians. The off-diagonal elements of \mathbf{L} will be anisotropic because of the anisotropy of the energy states split by the crystalline field. Therefore the magnetic moment possessed by a magnetic ion, and consequently the g -value, will be anisotropic.

Pryce (1950 a) has given a perturbational treatment of the above problem using the ingenious method of projection operators. Let us denote the energy levels split by the crystalline field as E_0 and E_i and take the perturbing Hamiltonian as

$$V = \lambda (\mathbf{L} \cdot \mathbf{S}) + \mu_B (\mathbf{L} \cdot \mathbf{H}), \quad (9.1)$$

where λ is the coefficient of the \mathbf{LS} coupling and \mathbf{H} represents the external field. Since the unperturbed states are independent of the spin state in the present case, we are able to treat spin \mathbf{S} as a parameter in the perturbational calculation. Accordingly, we can immediately get the second order perturbation energy as follows :

$$E_2 = - \sum_{i \neq 0} \frac{1}{E_i - E_0} \left| \sum_{\mu} \{ \lambda (i | L_{\mu} | 0) S_{\mu} + \mu_B (i | L_{\mu} | 0) H_{\mu} \} \right|^2,$$

where indices μ and ν represent Cartesian coordinates x , y and z . This can be written

$$E_2 = -2\lambda\mu_B \sum_{\mu, \nu} A_{\mu\nu} S_{\mu} H_{\nu} - \lambda^2 \sum_{\mu, \nu} A_{\mu\nu} S_{\mu} S_{\nu} - \mu_B^2 \sum_{\mu, \nu} A_{\mu\nu} H_{\mu} H_{\nu}, \quad . (9.2)$$

where

$$A_{\mu\nu} = \sum_{i \neq 0} \frac{(0 | L_{\mu} | i)(i | L_{\nu} | 0)}{E_i - E_0}. \quad (9.3)$$

The first term in (9.2) represents the contribution of the orbital magnetic moment and the second term the anisotropy energy which arises from the combination of the crystalline field and \mathbf{LS} coupling. The third term is spin-independent and gives rise to a temperature independent susceptibility which is generally anisotropic. If we add the unperturbed energy $E_0 + 2\mu_B \mathbf{SH}$ to (9.2), the effective Zeeman energy becomes

$$2\mu_B \sum_{\mu\nu} (\delta_{\mu\nu} - \lambda A_{\mu\nu}) S_{\mu} H_{\nu}, \quad (9.4)$$

which means that the effective g -value is generally a tensor of the form $2(1 - \lambda A)$, where 1 and A represent the matrices $(\delta_{\mu\nu})$ and $(A_{\mu\nu})$, and is real and symmetric because we can choose real unperturbed wave functions.

If we take the principal axes of this tensor as x -, y - and z -axes, the Zeeman energy and the anisotropy energy take, respectively, the forms

$$\mu_B (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) \quad . \quad . \quad . \quad (9.5)$$

and

$$-\lambda^2 A_x S_x^2 - \lambda^2 A_y S_y^2 - \lambda^2 A_z S_z^2. \quad . \quad . \quad . \quad (9.6)$$

Thus, the anisotropy constant per ion arising from the crystalline field is of the order of λ times $(g-2)$. If the crystalline field has cubic symmetry, the principal values of A become equal to each other and (9.5) and (9.6) become isotropic. Even then, anisotropy energy arises from a higher order perturbation as

$$A (S_x^4 + S_y^4 + S_z^4). \quad . \quad . \quad . \quad (9.7)$$

It should be noted that when the magnitude of S is equal to $\frac{1}{2}$, (9.6) and (9.7) simply reduce to constants; in this case the anisotropy energy does not arise from the anisotropy of the crystalline field.

9.2. Magnetic Dipolar Interaction and the Anisotropic Exchange Interaction

Next, we shall turn to the considerations on the anisotropic interactions between two spins. According to Kramers (1934) and van Vleck (1937 b), the interaction between spins l and m can be written

$$\sum_{\mu, \nu} C_{\mu\nu}^{(lm)} S_{l\mu} \cdot S_{m\nu}, \quad . \quad . \quad . \quad (9.8)$$

where $C_{\mu\nu}^{(lm)}$ is a real constant. As van Vleck has shown, this expression is the most general one when S is $\frac{1}{2}$, while for S larger than $\frac{1}{2}$ higher order interactions such as an interaction of the quadrupole type must be taken into account. This form of spin-spin interaction involves isotropic exchange interaction. To remove the isotropic part, the condition

$$\sum_{\mu} C_{\mu\mu}^{(lm)} = 0$$

is necessary.

The magnetic dipolar interaction between magnetic moments \mathbf{M}_l and \mathbf{M}_m ,

$$r_{lm}^{-3} (\mathbf{M}_l \cdot \mathbf{M}_m) - 3r_{lm}^{-5} (\mathbf{M}_l \cdot \mathbf{r}_{lm}) (\mathbf{M}_m \cdot \mathbf{r}_{lm}),$$

can be expressed in the form of (9.8), noticing that

$$\mathbf{M}_l = \mu_B \mathbf{g}_l \cdot \mathbf{S}_l \quad \text{and} \quad \mathbf{M}_m = \mu_B \mathbf{g}_m \cdot \mathbf{S}_m$$

by (9.4). That is, we get

$$C_{\mu\nu}^{(lm)} = \mu_B^2 \{ r_{lm}^{-3} (\mathbf{g}_{l,\mu} \cdot \mathbf{g}_{m,\nu}) - 3r_{lm}^{-5} (\mathbf{g}_{l,\mu} \cdot \mathbf{r}_{lm}) (\mathbf{g}_{m,\nu} \cdot \mathbf{r}_{lm}) \}, \quad (9.9a)$$

where \mathbf{r}_{lm} is the radius vector joining the l th to the m th ion and $\mathbf{g}_{l,\mu}$ and $\mathbf{g}_{m,\nu}$ are the vectors whose components are $(\mathbf{g}_{l,\mu x}, \mathbf{g}_{l,\mu y}, \mathbf{g}_{l,\mu z})$ and $(\mathbf{g}_{m,\nu x}, \mathbf{g}_{m,\nu y}, \mathbf{g}_{m,\nu z})$, respectively. The relation (9.9a) is equivalent to that derived by Opechowski (1948). For the case of an isotropic g -value, it naturally reduces to

$$C_{\mu\nu}^{(lm)} = g^2 \mu_B^2 r_{lm}^{-3} (\delta_{\mu\nu} - 3\mu_{lm}\nu_{lm}), \quad . \quad . \quad . \quad (9.9b)$$

where μ_{lm} and ν_{lm} are the direction cosines of \mathbf{r}_{lm} with respect to the μ - and ν -axes.

The anisotropic exchange interaction comes from the **LS** coupling and from an isotropic exchange interaction through the excited states and can be derived by a perturbational calculation. We shall take the system of two ions l and m and consider the energy states split by the crystalline field as the unperturbed states. The perturbing Hamiltonian of this two ion system will be given by

$$V = \lambda(\mathbf{L}_l \cdot \mathbf{S}_l) + \lambda(\mathbf{L}_m \cdot \mathbf{S}_m) + V_{\text{ex}}, \quad (9.10)$$

where the first and second terms are the **LS** couplings of ions l and m and V_{ex} means the isotropic exchange interaction. For simplicity, let us assume that V_{ex} has no off-diagonal element but has only diagonal elements in the excited states, which can be expressed as

$$(V_{\text{ex}})_{\text{diagonal element}} = -2J_e(\mathbf{S}_l \cdot \mathbf{S}_m), \quad (9.11)$$

where J_e is the exchange integral in that excited state. The perturbing Hamiltonian (9.10) has only off-diagonal elements connecting the ground state to those excited states of the two-ion system in which either of the two ions is excited to its higher level E_i and the remaining one is left in its ground state. In the present case, the unperturbed states are independent of spin orientations. Therefore, we may treat the spin operators in (9.10) and (9.11) as if they were mere parameters.

As we observe from the expressions for the perturbing Hamiltonian, (9.10) and (9.11), the anisotropic spin coupling between spins \mathbf{S}_l and \mathbf{S}_m occurs only in the third order. From (8.3) and (9.10), it can be seen that the most important terms included in the expression of the third order perturbation energy E_3 can be written

$$E_3 = \sum_i^l \frac{\langle 0 | \lambda(\mathbf{L}_l \cdot \mathbf{S}_l) | i \rangle \langle i | V_{\text{ex}} | i \rangle \langle i | \lambda(\mathbf{L}_l \cdot \mathbf{S}_l) | 0 \rangle}{(E_{li} - E_{l0})^2} + \sum_i^m \frac{\langle 0 | \lambda(\mathbf{L}_m \cdot \mathbf{S}_m) | i \rangle \langle i | V_{\text{ex}} | i \rangle \langle i | \lambda(\mathbf{L}_m \cdot \mathbf{S}_m) | 0 \rangle}{(E_{mi} - E_{m0})^2},$$

where E_{l0} , E_{li} and E_{m0} , E_{mi} represent the energies of the ground state and of the excited state of ions l and m , respectively, and \sum_i^l and \sum_i^m are taken over the excited states of ions l and m .

By use of (9.11), this expression can be written as

$$-2\lambda^2 \sum_{\mu, \nu} \Gamma_{\mu\nu}^l S_{l\mu}(\mathbf{S}_l \cdot \mathbf{S}_m) S_{l\nu} - 2\lambda^2 \sum_{\mu, \nu} \Gamma_{\mu\nu}^m S_{m\mu}(\mathbf{S}_l \cdot \mathbf{S}_m) S_{m\nu}, \quad (9.12)$$

where

$$\left. \begin{aligned} \Gamma_{\mu\nu}^l &= \sum_i^l J_{i0}^l \frac{\langle 0 | L_{l\mu} | i \rangle \langle i | L_{l\nu} | 0 \rangle}{(E_{li} - E_{l0})^2}; \\ \Gamma_{\mu\nu}^m &= \sum_i^m J_{i0}^m \frac{\langle 0 | L_{m\mu} | i \rangle \langle i | L_{m\nu} | 0 \rangle}{(E_{mi} - E_{m0})^2}. \end{aligned} \right\} \quad (9.13)$$

J_{i0}^l means the exchange integral between ion l in its i th excited level and ion m in its ground state, and J_{i0}^m has a similar meaning with l and m interchanged. $\Gamma_{\mu\nu}^l$ is a real symmetric tensor, since we can choose the unperturbed wave functions to be real.

For $S=\frac{1}{2}$, the following relations hold :

$$\begin{aligned} S_{lx}(\mathbf{S}_l \cdot \mathbf{S}_m)S_{lx} &= \frac{1}{2}S_{lx}S_{mx} - \frac{1}{4}(\mathbf{S}_l \cdot \mathbf{S}_m), \\ S_{lx}(\mathbf{S}_l \cdot \mathbf{S}_m)S_{ly} &= \frac{1}{4}S_{ly}S_{mx} + \frac{1}{4}S_{lx}S_{my} - (i/8)S_{mz}, \\ S_{ly}(\mathbf{S}_l \cdot \mathbf{S}_m)S_{lx} &= \frac{1}{4}S_{ly}S_{mx} + \frac{1}{4}S_{lx}S_{my} + (i/8)S_{mz}, \text{ etc.} \end{aligned}$$

(9.12) can be simplified to give

$$-\lambda^2 \sum_{\mu\nu} \left\{ \Gamma_{\mu\nu}^l - \frac{1}{3} \delta_{\mu\nu} \sum_{\lambda} \Gamma_{\lambda\lambda}^l \right\} S_{l\mu} S_{m\nu} - \lambda^2 \sum_{\mu\nu} \left\{ \Gamma_{\mu\nu}^m - \frac{1}{3} \delta_{\mu\nu} \sum_{\lambda} \Gamma_{\lambda\lambda}^m \right\} S_{l\mu} S_{m\nu}, \quad (9.14)$$

if we exclude the isotropic term. Therefore we obtain the following result for $S=\frac{1}{2}$:

$$C_{\mu\nu}^{(lm)} = \lambda^2 \left\{ \frac{1}{3} \delta_{\mu\nu} \sum_{\lambda} \Gamma_{\lambda\lambda}^l - \Gamma_{\mu\nu}^l \right\} + \lambda^2 \left\{ \frac{1}{3} \delta_{\mu\nu} \sum_{\lambda} \Gamma_{\lambda\lambda}^m - \Gamma_{\mu\nu}^m \right\}. \quad (9.15)$$

This result is equivalent to that originally derived by van Vleck (1951).

As we see from (9.3) and (9.13), $\Gamma_{\mu\nu}$ is of the same order of magnitude as $J A_{\mu\nu}^2$, since the off-diagonal elements of \mathbf{L} are of the order of unity, so that $J(g-2)^2$ gives the order of magnitude of the anisotropy energy per ion arising from the anisotropic exchange interaction. This fact was pointed out by Kittel (see van Vleck 1951). Thus we see that the anisotropy of the g -value is related to the anisotropy energy arising both from the crystalline field and from the anisotropic exchange interaction.

9.3. Anisotropy Constant below the Néel Temperature on the Basis of the Molecular Field Approximation

We have considered above three origins of the anisotropy in antiferromagnetic substances. These give the anisotropy energy of the spin system in the antiferromagnetic state as well as the anisotropy of the susceptibility above the Néel temperature.

In the antiferromagnetic state, the spin lattice is divided into two sublattices, one being occupied by plus spins and the other by minus spins. The direction of the common axis of these plus and minus spins with respect to the crystal axes cannot be determined by the isotropic exchange interaction. It is the anisotropic energy discussed above which determines this direction.

We denote the direction cosines of the plus and minus spins, respectively, as $(\alpha_+, \beta_+, \gamma_+)$ and $(\alpha_-, \beta_-, \gamma_-)$. We have $\alpha_+ = -\alpha_- \equiv \alpha$, $\beta_+ = -\beta_- \equiv \beta$ and $\gamma_+ = -\gamma_- \equiv \gamma$ when there is no external field, but these relations still hold approximately when the external field is present so long as the field is weak compared with the exchange field, which we shall assume. Now let us focus our attention on one spin only and employ the molecular field approximation. This spin is subjected to the average exchange field arising from the surrounding spins and is quantized in that direction. In the statistical average, the spin has a finite component in this direction but no component perpendicular to it. We introduce a new coordinate system ξ, η, ζ where the ζ -axis coincides with the direction of the exchange field. A part of the anisotropic energy given by (9.6), which can be written in the form

$$(A+B) S_z^2 - A S_x^2 - B S_y^2, \quad \dots \dots (9.16)$$

when the isotropic part is ignored, then becomes

$$\begin{aligned} & \{(A+B)n_1^2 - Al_1^2 - Bm_1^2\}S_\xi^2 + \{(A+B)n_1n_2 - Al_1l_2 - Bm_1m_2\}(S_\xi S_\eta + S_\eta S_\xi) \\ & + \{(A+B)n_2^2 - Al_2^2 - Bm_2^2\}S_\eta^2 + \{(A+B)n_1\gamma - Al_1\alpha - Bm_1\beta\}(S_\xi S_z + S_z S_\xi) \\ & + \{(A+B)\gamma^2 - A\alpha^2 - B\beta^2\}S_z^2 + \{(A+B)n_2\gamma - A\alpha l_2 - B\beta m_2\}(S_z S_\eta + S_\eta S_z), \end{aligned}$$

where (l_1, m_1, n_1) and (l_2, m_2, n_2) mean respectively the direction cosines of the ξ - and η -axes with respect to the x, y, z -coordinate system. In calculating the statistical average of this expression, we can put

$$\langle S_\xi^2 \rangle = \langle S_\eta^2 \rangle = \frac{1}{2}(S(S+1) - \langle S^2 \rangle),$$

$$\langle S_\xi S_z \rangle = \langle S_z S_\eta \rangle = 0, \text{ etc.},$$

the symbol $\langle \rangle$ representing the statistical average. Thus we get for the average anisotropic energy of one spin

$$\frac{1}{2}\{(A+B)\gamma^2 - A\alpha^2 - B\beta^2\}\{3\langle S_z^2 \rangle - S(S+1)\}, \quad . \quad . \quad . \quad (9.17)$$

where $\langle S_z^2 \rangle$ is given by

$$\sum_{m=-S}^S m^2 \exp(mg\mu_B H_e/kT) / \sum_{m=-S}^S \exp(mg\mu_B H_e/kT),$$

H_e being the magnitude of the exchange field. The sum of (9.17) over all the spins is the free energy arising from the orthorhombic part of the crystalline electric field. α, β, γ refer to the principal axes x, y, z of this field and A and B are given by (9.16).

From (9.17) we see that the temperature dependence of the anisotropy constant in this case is given by the factor of $3\langle S_z^2 \rangle - S(S+1)$, which becomes $S(2S-1)$ at the absolute zero of temperature and zero at the Néel temperature. It vanishes identically for $S=\frac{1}{2}$ because S_z^2 is always equal to $\frac{1}{4}$ for this case. The anisotropy energy coming from the cubic part can also be derived in a similar way.

Next we shall turn to the derivation of the anisotropy energy arising from the anisotropic interaction between spins, likewise on the basis of the molecular field approximation. This part of the anisotropy energy is the only non-vanishing part for $S=\frac{1}{2}$.

The energy of this interaction for the l -th spin on the plus sublattice is given by the sum of (9.8) over m , namely,

$$\sum_m \sum_{\mu, \nu} C_{\mu\nu}^{(lm)} S_{l\mu}^+ S_{m\nu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.18)$$

If we replace $S_{m\nu}$ by its average value, this becomes

$$\sum_{\mu\nu} a_{\mu\nu} S_{l\mu}^+ \langle \mathbf{S}^+ \rangle_\nu + \sum_{\mu\nu} c_{\mu\nu} S_{l\mu}^+ \langle \mathbf{S}^- \rangle_\nu, \quad . \quad . \quad . \quad (9.19)$$

where

$$a_{\mu\nu} = \sum_m C_{\mu\nu}^{(lm)} \quad \text{and} \quad c_{\mu\nu} = \sum_m C_{\mu\nu}^{(-lm)}. \quad . \quad . \quad . \quad . \quad (9.20)$$

The summations \sum_m^+ and \sum_m^- are taken over all the lattice points of the plus and minus sublattices, respectively. It can be seen that this energy is

equivalent to the magnetic energy of the plus spin subjected to an anisotropic molecular field whose μ th component, $H_{a\mu}^+$, is obtained by solving

$$\mu_B \sum_{\mu} g_{\mu\nu} H_{a\mu}^+ = \sum_{\mu} a_{\mu\nu} \langle \mathbf{S}^+ \rangle_{\mu} + \sum_{\mu} c_{\mu\nu} \langle \mathbf{S}^- \rangle_{\mu} \quad (9.21 a)$$

If the plus sublattice is equivalent to the minus sublattice, the anisotropic field for the spin of the minus sublattice is given similarly by

$$\mu_B \sum_{\mu} g_{\mu\nu} H_{a\mu}^- = \sum_{\mu} c_{\mu\nu} \langle \mathbf{S}^+ \rangle_{\mu} + \sum_{\mu} a_{\mu\nu} \langle \mathbf{S}^- \rangle_{\mu} \quad (9.21 b)$$

The anisotropy energy per spin pair arising from the interactions between spins is given by half the sum of the average values of (9.19) and the corresponding expression for the negative spin, namely,

$$\frac{1}{2} \sum_{\mu\nu} a_{\mu\nu} \{ \langle \mathbf{S}^+ \rangle_{\mu} \langle \mathbf{S}^+ \rangle_{\nu} + \langle \mathbf{S}^- \rangle_{\mu} \langle \mathbf{S}^- \rangle_{\nu} \} + \sum_{\mu\nu} c_{\mu\nu} \langle \mathbf{S}^- \rangle_{\mu} \langle \mathbf{S}^+ \rangle_{\nu} \quad (9.22)$$

Noticing that the direction cosines of $\langle \mathbf{S}^{\pm} \rangle$ are $(\pm\alpha, \pm\beta, \pm\gamma)$, this expression can be written as

$$\langle \mathbf{S} \rangle^2 \{ (a_{xx} - c_{xx})\alpha^2 + (a_{yy} - c_{yy})\beta^2 + (a_{zz} - c_{zz})\gamma^2 + 2(a_{xy} - c_{xy})\alpha\beta + 2(a_{yz} - c_{yz})\beta\gamma + 2(a_{zx} - c_{zx})\gamma\alpha \}, \quad (9.23)$$

where we have neglected the square of the difference between $\langle \mathbf{S}^+ \rangle$ and $\langle \mathbf{S}^- \rangle$ and put $\langle \mathbf{S} \rangle = \frac{1}{2}(\langle \mathbf{S}^+ \rangle + \langle \mathbf{S}^- \rangle)$. $\langle \mathbf{S} \rangle$ can be considered to be equal to the values of $\langle \mathbf{S}^+ \rangle$ and $-\langle \mathbf{S}^- \rangle$ for the case of no external field. The anisotropy constant in this case is thus proportional to the square of the spontaneous magnetization of each sublattice and shows therefore the same temperature dependence.

§ 10. ANISOTROPY ENERGY IN $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

The anisotropy constants of antiferromagnetic substances can be obtained from the measurements of antiferromagnetic resonance absorption, the field dependence of the Néel temperature or the value of the critical field for the flopping of spins. However, these observations are possible only when the external field is stronger than the geometrical mean of the anisotropy field and the exchange field. This geometrical mean amounts to more than 10^5 oersteds in ordinary antiferromagnetics and therefore the measurements of the anisotropy constants are usually impossible. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is the only substance whose magnetic properties have been thoroughly investigated and whose anisotropy constants have been determined. It has a Néel temperature of 4.3°K and consequently the exchange field is comparatively low; in fact, the observed critical field is in the neighbourhood of 7000 to 8500 oersteds. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, investigated quite recently at Leiden and at Washington, has a Néel temperature of 1.6°K , so that in this substance the determination of the anisotropy constants may also be possible.

Another method of deducing the value of the anisotropy constants, though indirect, is to observe the anisotropy of the susceptibility above the Néel temperature. This arises also from the three causes mentioned in the preceding section and affords certain information about the anisotropy constants below the Néel temperature. Stout, Griffel and Matarrese

have measured the anisotropy of the susceptibility above and below the Néel temperature in the rutile type antiferromagnetics, MnF_2 , FeF_2 and CoF_2 . From their results we can obtain information about the anisotropy energy below the Néel temperature, as we shall see in § 11.

In this section we shall consider the anisotropy energy of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

The crystal structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is orthorhombic, as shown in fig. 5 (a), 5 (b). The magnetic ions are subjected to the crystalline field arising from the surrounding charges and electric dipole moments, whose configuration for the corner ions is different from that for the face-centre ions, the former corresponding to the mirror image of the latter with respect to the ab -plane. This crystalline field seems to remove completely the directional degeneracy of the D -state of each free Cu^{2+} ion and consequently the orbital moment seems to be completely quenched in the ground state.

For each Cu^{2+} the crystalline electrostatic potential, which is not rigorously orthorhombic, can be expressed in ascending powers of x , y and z , i.e.,

$$Ax^2 - (A+B)y^2 + Bz^2 \pm Cxz + D(x^4 + y^4 + z^4) + E(x^4 + 6y^2z^2) \\ + G(y^4 + 6z^2x^2) \pm (Hx^2 + Kz^2 - 3(H+K)y^2)xz, \quad \dots \quad (10.1)$$

where plus and minus signs are taken for the corner ions and the face-centre ions, respectively. Terms higher than the fourth degree are not effective for the splitting of energy levels arising from d -orbitals, in which we are interested. From this expression for the crystalline potential we see that it does not mix real wave functions $(\phi_1 - \phi_{-1})/(\sqrt{2}i)$ and $(\phi_2 - \phi_{-2})/(\sqrt{2}i)$ with other real wave functions $(\phi_2 + \phi_{-2})/\sqrt{2}$, $(\phi_1 + \phi_{-1})/\sqrt{2}$ and ϕ_0 , where ϕ_0 , $\phi_{\pm 1}$, $\phi_{\pm 2}$ are the wave functions with $L=2$, $m=0, \pm 1$ and ± 2 , m being the z -component of the orbital angular momentum \mathbf{L} . Therefore the orbital wave functions of the Cu^{2+} ion in this crystalline field can be expressed as follows:—

$$\left. \begin{aligned} \Psi_0 &= A_0\phi_0 + A_{+2}(\phi_2 + \phi_{-2})/\sqrt{2} + A_{+1}(\phi_1 + \phi_{-1})/\sqrt{2}, \\ \Psi_1 &= B_0\phi_0 + B_{+2}(\phi_2 + \phi_{-2})/\sqrt{2} + B_{+1}(\phi_1 + \phi_{-1})/\sqrt{2}, \\ \Psi_2 &= C_0\phi_0 + C_{+2}(\phi_2 + \phi_{-2})/\sqrt{2} + C_{+1}(\phi_1 + \phi_{-1})/\sqrt{2}, \\ \Psi_3 &= D_{-1}(\phi_1 - \phi_{-1})/\sqrt{2}i + D_{-2}(\phi_2 - \phi_{-2})/\sqrt{2}i, \\ \Psi_4 &= E_{-1}(\phi_1 - \phi_{-1})/\sqrt{2}i + E_{-2}(\phi_2 - \phi_{-2})/\sqrt{2}i. \end{aligned} \right\} \quad \dots \quad (10.2)$$

A_i , B_i , C_i , D_i and E_i are real constants to be determined by the coefficients of the crystalline potential. We now regard such non-degenerate wave functions as unperturbed wave functions and their energies, E_0 , E_1 , \dots , E_4 , as unperturbed energies. Then, introducing \mathbf{LS} coupling and exchange interactions between ions as perturbing Hamiltonian, we obtain the anisotropy of the g -value and the coefficients of the anisotropic exchange interaction by the procedure developed in the preceding section. The anisotropy energy discussed in § 9.1 does not appear in this case, because the Cu^{2+} ion has a spin of $\frac{1}{2}$.

We shall first discuss the anisotropy of the g -value, assuming that the ground state corresponds to Ψ_0 , as predicted from the cases of other crystals containing Cu^{2+} ions. The matrix elements of L_x , L_y and L_z between the unperturbed wave functions (10.2) can easily be calculated as follows :

$$\left. \begin{aligned} (0 | L_z | 1) &= (0 | L_z | 2) = 0, \\ (0 | L_z | 3) &= -i(A_{+1}D_{-1} + 2A_{+2}D_{-2}), \\ (0 | L_z | 4) &= -i(A_{+1}E_{-1} + 2A_{+2}E_{-2}), \end{aligned} \right\} \quad . \quad . \quad . \quad (10.3a)$$

$$\left. \begin{aligned} (0 | L_x | 1) &= (0 | L_x | 2) = 0, \\ (0 | L_x | 3) &= i(3A_0D_{-1} + A_{+2}D_{-1} + A_{+1}D_{-2}), \\ (0 | L_x | 4) &= i(3A_0E_{-1} + A_{+2}E_{-1} + A_{+1}E_{-2}), \end{aligned} \right\} \quad . \quad . \quad . \quad (10.3b)$$

$$\left. \begin{aligned} (0 | L_y | 1) &= -i(3A_0B_{+1} - A_{+2}B_{+1} + A_{+1}B_{+2}), \\ (0 | L_y | 2) &= -i(3A_0C_{+1} - A_{+2}C_{+1} + A_{+1}C_{+2}), \\ (0 | L_y | 3) &= (0 | L_y | 4) = 0. \end{aligned} \right\} \quad . \quad . \quad . \quad (10.3c)$$

Inserting these values of the matrix elements into (9.3), we get $A_{\mu\nu}$. In particular, we have $A_{xy} = A_{yz} = 0$. Since the g -tensor is $2(1 - \lambda A)$, as we have seen in (9.4), we see that one of the principal axes, η , of this tensor coincides with the b or y -axis, and the remaining ξ and ζ -axes make an angle α with the a and c -axes, respectively. We also see that the angle α for the corner ions has the opposite sign to that for the face-centre ions. The principal values g_ξ and g_ζ of the g -tensor and the angle α between the ξ -axis and the a -axis are given by

$$g_\xi = \frac{1}{2}[g_{xx} + g_{zz} - \{(g_{xx} - g_{zz})^2 + 4g_{xz}^2\}^{\frac{1}{2}}], \quad . \quad . \quad . \quad . \quad (10.4)$$

$$g_\zeta = \frac{1}{2}[g_{xx} + g_{zz} + \{(g_{xx} - g_{zz})^2 + 4g_{xz}^2\}^{\frac{1}{2}}], \quad . \quad . \quad . \quad . \quad (10.5)$$

$$\sin(2\alpha) = \pm 2g_{xz} / \{(g_{xx} - g_{zz})^2 + 4g_{xz}^2\}^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (10.6)$$

The above calculations are similar to those which Polder (1942) has done in his paper on the anisotropy of the susceptibility of $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

The Zeeman energy for an anisotropic g -value is represented by $\mu_B \mathbf{SgH}$ and so its eigenvalues for $S = \frac{1}{2}$ can be obtained by solving the following secular equation :

$$\begin{vmatrix} \frac{1}{2}\mu_B(g_{zx}H_x + g_{zy}H_y + g_{zz}H_z) - \epsilon & \frac{1}{2}\mu_B\{g_{xx}H_x + g_{xy}H_y + g_{xz}H_z\} \\ & -i(g_{yx}H_x + g_{yy}H_y + g_{yz}H_z)\} \\ \frac{1}{2}\mu_B\{g_{xx}H_x + g_{xy}H_y + g_{xz}H_z\} & -\frac{1}{2}\mu_B(g_{zx}H_x + g_{zy}H_y + g_{zz}H_z) - \epsilon \\ & +i(g_{yx}H_x + g_{yy}H_y + g_{yz}H_z)\} \end{vmatrix} = 0 \quad (10.7)$$

which gives

$$\epsilon = \pm \frac{1}{2}\mu_B \{ (g_{xx}H_x + g_{xy}H_y + g_{xz}H_z)^2 + (g_{yx}H_x + g_{yy}H_y + g_{yz}H_z)^2 + (g_{zx}H_x + g_{zy}H_y + g_{zz}H_z)^2 \}^{\frac{1}{2}}. \quad . \quad . \quad . \quad (10.8)$$

Now if we write the direction cosines of \mathbf{H} as α_H , β_H , γ_H , (10.8) becomes

$$\epsilon = \pm \frac{1}{2}\mu_B H \{ (g_{xx}\alpha_H + g_{xy}\beta_H + g_{xz}\gamma_H)^2 + (g_{yx}\alpha_H + g_{yy}\beta_H + g_{yz}\gamma_H)^2 + (g_{zx}\alpha_H + g_{zy}\beta_H + g_{zz}\gamma_H)^2 \}^{\frac{1}{2}};$$

therefore we obtain for the effective g -value

$$g_{\text{eff}} = \{ (g_{xx}\alpha_H + g_{xy}\beta_H + g_{xz}\gamma_H)^2 + (g_{yx}\alpha_H + g_{yy}\beta_H + g_{yz}\gamma_H)^2 + (g_{zx}\alpha_H + g_{zy}\beta_H + g_{zz}\gamma_H)^2 \}^{\frac{1}{2}}. \quad (10.9)$$

For the present case, $g_{xy} = g_{yz} = 0$, so that the effective g -values for the cases where the external field is applied along each of the crystal axes are

$$\left. \begin{aligned} g_a &= (g_{xx}^2 + g_{zz}^2)^{\frac{1}{2}} = (g_{\xi}^2 \cos^2 \alpha + g_{\zeta}^2 \sin^2 \alpha)^{\frac{1}{2}}, \\ g_b &= g_{yy}, \\ g_c &= (g_{xx}^2 + g_{zz}^2)^{\frac{1}{2}} = (g_{\xi}^2 \sin^2 \alpha + g_{\zeta}^2 \cos^2 \alpha)^{\frac{1}{2}}. \end{aligned} \right\} \quad (10.10)$$

These values can be obtained either from experiments on paramagnetic resonance absorption or from susceptibility measurements at temperatures sufficiently above the Néel temperature. The former experiments have been done by Itoh, Fujimoto and Ibamoto (1951) and the latter by van den Handel, Gijsman and Poulis (1952). The values they obtained are cited in § 6. To obtain these values theoretically, we must know the numerical details of the crystalline field, for which we have at present no reliable data.

The ordinary dipolar energy can be obtained easily by use of the above experimental g -values, whereas the evaluation of the anisotropic exchange energy is rather difficult, because we have to evaluate Γ_{uv} given by (9.13) which requires detailed knowledge of the crystalline field. For this reason Moriya and Yosida (1953) and independently Keffer (1953) estimated the anisotropy constants of the substance under consideration on the basis of much simplified assumptions.

Moriya and Yosida assumed that the ξ -axis coincides with the line joining a Cu^{2+} ion to its nearest Cl^- ion. This assumption gives $\cos^2 \alpha = 0.6425$. Using this value, and the experimental g -value, they estimated the principal g -values to be

$$g_{\xi} = 2.111, \quad g_{\eta} = 2.075 \quad \text{and} \quad g_{\zeta} = 2.339. \quad (10.11)$$

They further assumed that the crystalline field has an orthorhombic symmetry with axes coinciding with the principal axes of the g -tensor, namely, ξ , η and ζ . Then the following splitting of the energy level can be derived:

$$\left. \begin{aligned} \Psi_a &= A_2 (\phi_2 + \phi_{-2}) / \sqrt{2} + A_0 \phi_0 : E_a, \\ \Psi_b &= B_2 (\phi_2 + \phi_{-2}) / \sqrt{2} + B_0 \phi_0 : E_b, \\ \Psi_4 &= (\phi_2 - \phi_{-2}) / \sqrt{2} i : E_1, \\ \Psi_2 &= (\phi_1 + \phi_{-1}) / \sqrt{2} : E_2, \\ \Psi_5 &= (\phi_1 - \phi_{-1}) / \sqrt{2} i : E_5. \end{aligned} \right\} \quad (10.12)$$

For this simplified case, (9.3) gives the following g -values:

$$\left. \begin{aligned} g_{\xi} &= 2\{1 - \gamma_5(A_2 + \sqrt{3}A_0)^2\}, \\ g_{\eta} &= 2\{1 - \gamma_2(A_2 - \sqrt{3}A_0)^2\}, \\ g_{\zeta} &= 2(1 - 4\gamma_4 A_2^2), \end{aligned} \right\} \quad (10.13)$$

where

$$\gamma_i = \lambda / (E_i - E_a). \quad (10.14)$$

Equating (10.11) with (10.13), we obtain the following relations :

$$\left. \begin{aligned} 4\gamma_4^2 A_2^4 &= 7.174 \times 10^{-3}, & \gamma_5^2 (A_2 + \sqrt{3}A_0)^4 &= 3.056 \times 10^{-3}, \\ \gamma_2^2 (A_2 - \sqrt{3}A_0)^4 &= 1.406 \times 10^{-3}. \end{aligned} \right\} \quad (10.15)$$

Since the crystalline field is not known, the problem was further simplified by putting $A_2 \sim 1$ and $A_0 \sim 0$, which seems to be reasonable, because it is equivalent to putting $g_\xi = g_\eta$ (see (10.11)). Finally, to evaluate the coefficient $\Gamma_{\mu\nu}$ represented by (9.13), all the exchange integrals for one ion in the excited state and the other in the ground state were put equal to the exchange integrals for both in the ground state. The exchange integrals then appeared in a combined form $\Sigma^{++} J_{++} - \Sigma^{+-} J_{+-}$, where plus and minus represent the species of the sublattices and the summations are extended over the interacting neighbours. This corresponds to the coefficient of the Weiss field and so could be estimated from the Néel temperature. Having thus estimated the values of $\Gamma_{\mu\nu}$, they calculated the anisotropy energy arising from the anisotropic exchange interaction, using (9.15), (9.20) and (9.23) and referring to the spin superstructure obtained by Poulis and Hardeman (1952 a) from proton resonance absorption (fig. 5 (a)). The result for the anisotropy energy was

$$E_a = \kappa_1 \beta^2 + \kappa_2 \gamma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.16)$$

with

$$\kappa_1 = 4.5 \times 10^{-3} \text{ cm}^{-1} \quad \text{and} \quad \kappa_2 = -1.7 \times 10^{-3} \text{ cm}^{-1} \quad . \quad . \quad (10.17)$$

per Cu ion at the absolute zero of temperature.

To the result above we have to add the anisotropy constants arising from the dipolar interactions between spins, which is given by (9.9) and (9.23). For these, we must sum the dipolar part of $C_{\mu\nu}^{(lm)}$ over all the lattice points m . The summation can be carried out by use of Ewald-Kornfeld's method, as has been done by Keffer (1952) for the crystal of MnF_2 , to which we shall refer later. The result obtained by Moriya and Yosida (1953), assuming an isotropic g -value of 2, was

$$\kappa_1 = -0.27 \times 10^{-3} \text{ cm}^{-1} \quad \text{and} \quad \kappa_2 = 29.1 \times 10^{-3} \text{ cm}^{-1} \quad . \quad (10.18)$$

However, when the anisotropy of the g -value, obtained experimentally, was introduced, these values were altered to

$$\kappa_1 = 0.93 \times 10^{-3} \text{ cm}^{-1} \quad \text{and} \quad \kappa_2 = 36.4 \times 10^{-3} \text{ cm}^{-1} \quad . \quad (10.19)$$

The total anisotropy constants are given by the sum of (10.19) and (10.17), namely,

$$\kappa_1 = 5.43 \times 10^{-3} \text{ cm}^{-1} \quad \text{and} \quad \kappa_2 = 34.7 \times 10^{-3} \text{ cm}^{-1} \quad . \quad (10.20)$$

The experimental values to be compared with these calculated values are

$$\kappa_1 = 5.1 \times 10^{-3} \text{ cm}^{-1} \quad \text{and} \quad \kappa_2 = 16.8 \times 10^{-3} \text{ cm}^{-1} \quad . \quad (10.21)$$

(10.21) has been derived as follows. The analysis of antiferromagnetic resonance observations described in § 6 gives the values of $2AK_1$ and $2AK_2$, where A means the molecular field constant arising from the

isotropic exchange interaction between the plus and minus spins and K_1 and K_2 are, respectively, the anisotropy constants per unit volume in the ab and ac -planes. Their values are

$$2AK_1 = 5.11 \times 10^7 \text{ oe}^2, \quad K_2/K_1 = 3.3. \quad . \quad . \quad . \quad (10.22)$$

Combining these values with the value of A estimated from the perpendicular susceptibility at a temperature sufficiently below the Néel point ($A^{-1} = \chi_{\perp} = 1.40 \times 10^{-4}$), we have (10.21). We might remark here that the value of A estimated from the Néel temperature, neglecting Γ (see (4.13)), is considerably smaller than that evaluated from χ_{\perp} .

Comparing (10.20) with (10.21) we see a good agreement between the experimental and theoretical values of κ_1 but a rather poor agreement for κ_2 , the theoretical value being nearly twice as large as the experimental one. This discrepancy may be due to the crude assumptions made in the theoretical derivation of the anisotropy constants originating from anisotropic exchange interaction. But it should be remarked that the value of κ_1 arises mainly from the latter, while for κ_2 the magnetic dipole-dipole interaction contributes the greater part.

§ 11. ANISOTROPY ENERGY IN MnF_2 , FeF_2 , AND CoF_2

Stout and Griffel (1949), Griffel and Stout (1950) and Stout and Matarrese (1953) have measured the anisotropic susceptibility above the Néel temperature in single crystals of MnF_2 , FeF_2 and CoF_2 , which have a structure of the rutile type. From these measurements we can draw some information about their anisotropy energies.

In crystals of the rutile type the metallic ions constitute a body-centred tetragonal lattice and each is surrounded nearly octahedrally by six negative ions. The crystalline field at each metallic ion is therefore orthorhombic, and the principal axes, ξ , η and ζ of the field at each of the corner ions are in the directions $[110]$, $[\bar{1}10]$ and $[001]$, respectively, whilst at each of the body-centre ions they are in the directions $[\bar{1}10]$, $[110]$ and $[001]$, respectively. The electrostatic potential of such a crystalline field can be expressed in powers of ξ , η and ζ as follows :

$$A\xi^2 + B\eta^2 - (A+B)\zeta^2 + D(\xi^4 + \eta^4 + \zeta^4) + F(\xi^4 + 6\eta^2\zeta^2) + G(\eta^4 + 6\xi^2\zeta^2), \\ . \quad . \quad . \quad . \quad (11.1)$$

where we have written the terms up to the fourth power, since only these are effective for the splitting of the energy levels of the d -electrons. This crystalline field produces the anisotropy of the g -value, as well as the anisotropic energy, which is expressible as a function of the spin \mathbf{S} of one ion and the anisotropic exchange interaction, as mentioned in § 9.

MnF_2

The anisotropy of MnF_2 has been studied by Yosida (1951) and Keffer (1952). In particular, Keffer concluded that the main part of the anisotropy energy of this substance is accounted for by the magnetic dipolar energy.

The free state of Mn^{2+} is ${}^6S(3d)^5$. Therefore, there is no orbital degeneracy. However, van Vleck and Penney (1934) have shown that the configurational interaction due to the combined action of the crystalline field (11.1) and the spin-orbit coupling gives rise to anisotropy energy of the form of (9.6), while Pryce (1950 b) and Abragam and Pryce (1951) pointed out that in paramagnetic salts the dipolar interaction between electronic spins within the same Mn^{2+} ion is more important than the spin-orbit coupling. In either case we can expect in this crystal the following type of anisotropic energy :

$$\left. \begin{aligned} D_{\xi}S_{\xi}^2 + D_{\eta}S_{\eta}^2 - (D_{\xi} + D_{\eta})S_{\xi}^2 & \quad \text{for the corner ion,} \\ D_{\eta}S_{\xi}^2 + D_{\xi}S_{\eta}^2 - (D_{\xi} + D_{\eta})S_{\xi}^2 & \quad \text{for the body-centre ion.} \end{aligned} \right\} \quad (11.2)$$

The sum of these two expressions is actually important for the anisotropy energy and the value of $D = \frac{3}{2}(D_{\xi} + D_{\eta})$ has been estimated by Keffer (1952) by assuming the relation

$$\frac{D(\text{MnF}_2)}{D(\text{Tutton})} = \frac{A(\text{MnF}_2) + B(\text{MnF}_2)}{A(\text{Tutton}) + B(\text{Tutton})},$$

where A and B mean the coefficients of the quadratic terms of (11.1). He used the rough values of A and B calculated by himself for MnF_2 and those calculated by Polder (1942) for the Tutton salt and also the value of D for manganese ammonium Tutton salt deduced from paramagnetic resonance absorption. The value of D estimated in this way for MnF_2 was found to be 0.012 cm^{-1} , which was much smaller than that necessary to account for the experimental value of the anisotropy of the susceptibility.

The fact that the observed g -value is almost equal to 2 indicates that the anisotropic exchange interaction, whose order of magnitude is given by $J(g-2)^2$, is also small.

The anisotropy energy arising from the magnetic dipole-dipole interaction has been calculated by Keffer (1952) using the superstructure of spins determined by neutron diffraction study by Erickson and Shull (1951) and Erickson (1953). Apparently the corner sites are occupied by plus spins and the body-centre sites by minus spins. The internal anisotropic field represented by (9.21 *a*) and (9.21 *b*) is, therefore,

$$H_{a\mu}^{\pm} = \sum_{\nu} \Phi_{\mu\nu}' M_{\nu}^{\pm} + \sum_{\nu} \Phi_{\mu\nu}'' M_{\nu}^{\mp}, \quad \dots \quad (11.3)$$

$\Phi_{\mu\nu}'$ and $\Phi_{\mu\nu}''$ being given by the following lattice sums :

$$\left. \begin{aligned} \Phi_{\mu\nu}' &= -(2/N) \sum_m^+ r_{lm}^{-3} (\delta_{\mu\nu} - 3\mu_{lm}\nu_{lm}), \\ \Phi_{\mu\nu}'' &= -(2/N) \sum_m^- r_{lm}^{-3} (\delta_{\mu\nu} - 3\mu_{lm}\nu_{lm}). \end{aligned} \right\} \quad \dots \quad (11.4)$$

Since the spin lattice is tetragonal in the present case, the non-diagonal components of these Φ 's vanish when referred to the crystal axes. The values of the diagonal components calculated by Keffer are as follows :

$$\Phi_c' - \Phi_a' = 9.25, \quad \Phi_c'' - \Phi_a'' = -4.85. \quad \dots \quad (11.5)$$

If we introduce (11.3) as a part of the internal field, the magnetic moments of the two sublattices above the Néel temperature can be obtained from

$$M^{\pm} = (C/T)(H - AM^{\mp} - \Gamma M^{\pm} + \Phi' M^{\pm} + \Phi'' M^{\mp}), \quad \dots \quad (11.6)$$

where C means the Curie-Weiss constant (see § 4 for the molecular field formalism). From these equations the susceptibilities parallel and perpendicular to the c -axis are obtained, i.e.,

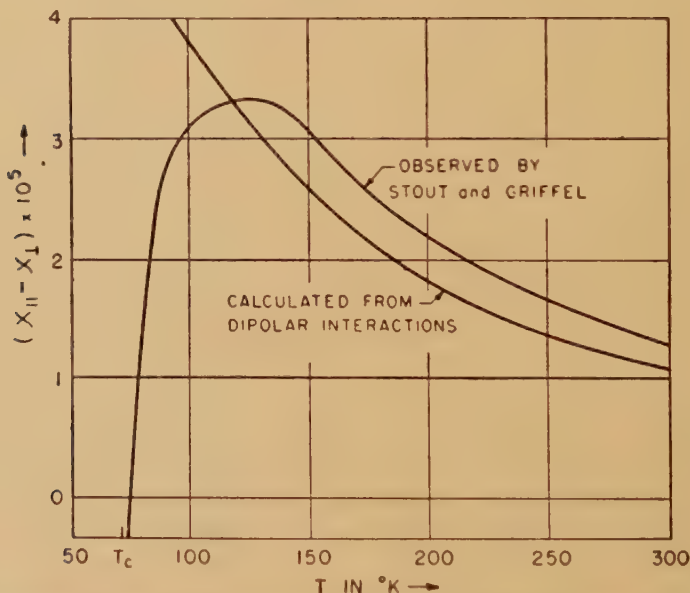
$$\left. \begin{aligned} \chi_c &= C / \{T + \frac{1}{2}C(A + \Gamma - \Phi_c' - \Phi_c'')\}, \\ \chi_a &= C / \{T + \frac{1}{2}C(A + \Gamma - \Phi_a' - \Phi_a'')\}. \end{aligned} \right\} \quad \dots \quad (11.7)$$

These equations lead to

$$\chi_c - \chi_a = \frac{1}{2}\chi_a\chi_c(\Phi_c' - \Phi_a' + \Phi_c'' - \Phi_a''), \quad \dots \quad (11.8)$$

which is positive. Keffer calculated this difference as a function of temperature by using (11.5) and replacing $\chi_a\chi_c$ by the square of the powder susceptibility. The latter has been given experimentally by Bizette and Tsai (1939). The results are shown in fig. 27 together with experimental

Fig. 27



The anisotropy in the molal susceptibility of MnF_2 above the Néel temperature. Observation after Stout and Griffel (1950) and calculation after Keffer (1952).

values for $\chi_c - \chi_a$ obtained by Griffel and Stout (1950). This figure shows that the major part of the anisotropy can be accounted for in terms of the magnetic dipolar energy. The small difference between these two curves may be due to the anisotropy energy of (11.2).

The anisotropy energy arising from this magnetic dipolar interaction can be expressed, as seen from (9.23), as

$$E_a = -M_0^2 \{(\Phi_c' - \Phi_a') - (\Phi_c'' - \Phi_a'')\} \gamma^2. \quad \dots \quad (11.9)$$

The values given in (11.5) show that the coefficient of γ^2 is negative, so that the preferred axis coincides with the c -axis. This is in accord with the results of neutron diffraction. Therefore, the susceptibility along this direction, χ_c , corresponds to χ_{11} of the van Vleck theory and that perpendicular to this direction, χ_a , corresponds to χ_{11} . Thus, below the Néel temperature, χ_c becomes smaller than χ_a . When the temperature is lowered, the experimental curve in fig. 27 deviates from the theoretical curve near the Néel temperature and cuts the temperature axis just above the Néel temperature. This behaviour must be due to the short range order which should exist above the Néel point but which has been neglected in the present molecular field approximation.

At absolute zero, the magnetization of each sublattice, M_0 , becomes equal to the absolute saturation magnetization given by $(N/2) g\mu_B S$. Using the latter value, Keffer estimated the magnitude of the dipolar anisotropy field at absolute zero to be 8300 oersteds. Combining this with the contributions from other sources then Keffer obtained a total anisotropy field of 8800 oersteds. This gives rise to a value of the critical field, H_c , of 1.0×10^5 oersteds (see also the value on p. 40).

It is interesting to compare the anisotropy energy of MnF_2 with that of MnO_2 which is also of the rutile type. The spin superstructure of MnO_2 studied by Erickson (1952) was referred to in § 2. For that superstructure, the contribution of the magnetic dipolar interaction to the anisotropy energy is entirely different from that for MnF_2 . The results obtained by Yosida (1952 c) are as follows :

$$\left. \begin{aligned} \chi_c - \chi_a &= 2.86 \chi_c \chi_a, \\ E_a &= 21.46 M_0^2 (\gamma_1^2 + \gamma_3^2), \end{aligned} \right\} \quad . \quad . \quad . \quad (11.10)$$

where γ_1 and γ_3 mean the direction cosines to the c -axis of the common axes of spins, for the corner lattice and for the body-centre lattice respectively. In this case the dipolar energy gives a positive value of $\chi_c - \chi_a$ above the Néel temperature, while below the Néel temperature it confines the spins to the plane perpendicular to the c -axis, so that again $\chi_c - \chi_a$ is positive. This result agrees with the behaviour of the susceptibility of the single crystal of MnO_2 , given in Bizette's article (1951). However, the manganese ions in MnO_2 are Mn^{4+} and the free Mn^{4+} ion is in the state 4F , so that the anisotropy energy of the type of (9.6), which arises from the anisotropy of the crystalline field, would give a considerable part of the anisotropy energy of this substance. This energy can be expressed as

$$\begin{aligned} -\lambda^2 A_\xi S_\xi^2 - \lambda^2 A_\eta S_\eta^2 - \lambda^2 A_\zeta S_\zeta^2 & \quad \text{for the corner ion,} \\ -\lambda^2 A_\eta S_\xi^2 - \lambda^2 A_\xi S_\eta^2 - \lambda^2 A_\zeta S_\zeta^2 & \quad \text{for the body-centre ion.} \end{aligned}$$

Then, corresponding to the experimental fact that $\chi_c - \chi_a$ is positive both above and below the Néel temperature, it is expected that A_ζ should be larger than $\frac{1}{2}(A_\xi + A_\eta)$ and less than the larger of A_ξ and A_η . Thus, below the Néel temperature the spins would point in the direction of the principal axis that corresponds to the largest value of A in the plane perpendicular to

the c -axis and the direction of the corner spins would be perpendicular to that of the body-centre spins.

FeF₂

According to the experiments of Stout and Matarrese (1953), the anisotropy of the susceptibility of FeF₂ is similar to that of MnF₂, and $\chi_c - \chi_a$ changes sign near the Néel temperature (see fig. 11). This is consistent with the results of a neutron diffraction experiment by Erickson (1953) who showed that the superstructure of this substance is the same as that of MnF₂, the preferred axis of spins coinciding with the c -axis. However, the difference of χ_c and χ_a above the Néel temperature is greater than that for MnF₂ by a factor of 100. Stout and Matarrese suggested that this large anisotropy originates from the crystalline field, because a free Fe²⁺ ion is in the state ⁵D.

Niira and Oguchi (1954) analysed the experimental data of Stout and Matarrese and confirmed that the magnetic anisotropy of this substance can be accounted for by the anisotropy of the crystalline field acting on the Fe²⁺ ions.

The directional degeneracy of the orbital state of a single Fe²⁺ ion is completely removed by the orthorhombic crystalline field (11.1). Assuming the energy differences between two levels to be large compared with kT , the effective Hamiltonian of the ground state can be obtained from (9.4), (9.5) and (9.6), as

$$2\mu_B(1-\lambda A_\xi)S_\xi H_\xi + 2\mu_B(1-\lambda A_\eta)S_\eta H_\eta + 2\mu_B(1-\lambda A_\zeta)S_\zeta H_\zeta \\ - \lambda^2 A_\xi S_\xi^2 - \lambda^2 A_\eta S_\eta^2 - \lambda^2 A_\zeta S_\zeta^2 \text{ (for the corner ion) } \quad (11.11 a)$$

and

$$2\mu_B(1-\lambda A_\eta)S_\xi H_\xi + 2\mu_B(1-\lambda A_\xi)S_\eta H_\eta + 2\mu_B(1-\lambda A_\zeta)S_\zeta H_\zeta \\ - \lambda^2 A_\eta S_\xi^2 - \lambda^2 A_\xi S_\eta^2 - \lambda^2 A_\zeta S_\zeta^2, \text{ (for the body-centre ion) } \quad (11.11 b)$$

where ξ , η and ζ denote the principal axes of the crystalline field acting on the corner ion. The terms quadratic in S_ξ , S_η and S_ζ in these expressions can be written in another form, apart from a constant term, as

$$D_\xi S_\xi^2 + D_\eta S_\eta^2 - (D_\xi + D_\eta) S_\zeta^2, \quad (11.12)$$

$$\left. \begin{aligned} D_\xi &= -\lambda^2(2A_\xi - A_\eta - A_\zeta)/3 = \lambda(2g_\xi - g_\eta - g_\zeta)/6, \\ D_\eta &= -\lambda^2(2A_\eta - A_\xi - A_\zeta)/3 = \lambda(2g_\eta - g_\xi - g_\zeta)/6, \end{aligned} \right\} \quad (11.13)$$

for the corner ion and the same expression with D_ξ exchanged with D_η for the body-centre ion. Both the susceptibilities χ_c and χ_a obey the Curie-Weiss law fairly well and so we can estimate the effective g -value from the tangent of the graph of the reciprocal susceptibility versus temperature. The values estimated by Niira and Oguchi are

$$g_\zeta = 2.45 \text{ and } \{(g_\xi^2 + g_\eta^2)/2\}^\dagger = 2.24. \quad (11.14)$$

Since it is impossible to estimate the values of g_ξ and g_η separately, without knowing the crystalline field, one may put $g_\xi \sim g_\eta$. Then the value of $D_\xi + D_\eta$ can be estimated to be

$$D_\xi + D_\eta \approx -\lambda(g_\zeta - g_\xi)/3 \approx 6.7 \text{ cm}^{-1}.$$

This value is very large compared to the corresponding value for MnF_2 and therefore we can expect a large anisotropy to arise from the crystalline field.

The total Hamiltonian of the spin system of this substance is written

$$\begin{aligned}\mathcal{H}_{\text{tot}} = & 2J\sum_{k,j} \mathbf{S}_k \cdot \mathbf{S}_j + \sum_j \{ \mu_B (g_\xi S_{j\xi} H_\xi + g_\eta S_{j\eta} H_\eta + g_\zeta S_{j\zeta} H_\zeta) \\ & + D_\xi S_{j\xi}^2 + D_\eta S_{j\eta}^2 + D_\zeta S_{j\zeta}^2 \} + \sum_k \{ \mu_B (g_\eta S_{k\xi} H_\xi + g_\xi S_{k\eta} H_\eta + g_\zeta S_{k\zeta} H_\zeta) \\ & + D_\eta S_{k\xi}^2 + D_\xi S_{k\eta}^2 + D_\zeta S_{k\zeta}^2 \}, \quad (D_\zeta = -D_\xi - D_\eta) \quad \dots \quad (11.15)\end{aligned}$$

where indices j and k denote the corner and body-centre ions, respectively. The susceptibilities χ_a and χ_c above the Néel temperature are obtained most simply by the method of diagonal sums developed by van Vleck (1937 a) and Opechowski (1937). The result of the expansion up to the second power of $1/kT$ is as follows :

$$\chi_c = \frac{N\mu_B^2 S(S+1)g_\zeta^2}{3kT'} \left[1 - \frac{2JzS(S+1)}{3kT'} + \frac{3(D_\xi + D_\eta)}{kT'} \left\{ \frac{2S(S+1)}{15} - \frac{1}{10} \right\} \right], \quad \dots \quad (11.16)$$

$$\begin{aligned}\chi_a = & \frac{N\mu_B^2 S(S+1)(g_\xi^2 + g_\eta^2)}{6kT'} \left[1 - \frac{4JzS(S+1)g_\xi g_\eta}{3kT'(g_\xi^2 + g_\eta^2)} \right. \\ & \left. - \frac{3(g_\xi^2 D + g_\eta^2 D_\eta)}{kT'(g_\xi^2 + g_\eta^2)} \left\{ \frac{2S(S+1)}{15} - \frac{1}{10} \right\} \right], \quad \dots \quad (11.17)\end{aligned}$$

and the difference of these two expressions can be written

$$\begin{aligned}\chi_c - \chi_a = & \frac{4N\mu_B S(S+1)}{3kT' + 2JzS(S+1)} \left[\frac{1}{4} \{ g_\zeta^2 - \frac{1}{2}(g_\xi^2 + g_\eta^2) \} - \frac{2JzS(S+1)}{3kT'} \left(\frac{g_\xi - g_\eta}{2} \right)^2 \right. \\ & \left. + \frac{3}{2kT'} \left\{ \frac{2S(S+1)}{15} - \frac{1}{10} \right\} \left\{ \frac{1}{2} g_\zeta^2 (D_\xi + D_\eta) + \frac{1}{4} (g_\xi^2 D_\xi + g_\eta^2 D_\eta) \right\} \right]. \quad \dots \quad (11.18)\end{aligned}$$

Putting (11.14) and $g_\xi = g_\eta$ into this expression, we obtain a large value of the anisotropy in the susceptibility, which agrees in order of magnitude with the experimental result. The contribution from the anisotropic exchange interaction should be considerably smaller than this, since the order of its magnitude is given by $J(g-2)^2$ while that of the anisotropic energy arising from the crystalline field is given by $\lambda(g-2)$ as seen from (9.2).

Below the Néel temperature the anisotropy energy arising from the crystalline field is given by (9.17). The value of $D_\xi + D_\eta$ is about 6.7 cm^{-1} , as estimated above. Therefore the anisotropy energy of this substance should be very large at low temperatures, the anisotropy field at the absolute zero of temperature amounting to $10^4 \sim 10^5 \text{ oe}$.

In CoF_2 , the difference between the two principal susceptibilities is also very large. However, this difference, $\chi_c - \chi_a$, shows a somewhat different behaviour from that in FeF_2 ; it is positive at high temperatures

but changes its sign at 150°K, that is, at a temperature considerably higher than the Néel temperature of 37.7°K at which an anomaly of the specific heat is observed (see fig. 12).

Recently Nakamura and Taketa (1954) explained the magnetic behaviour of CoF_2 , taking into consideration only the lowest orbital level which has a four-fold spin degeneracy. This level is split by the crystalline anisotropy energy (9.6) into two Kramers doublets. They assumed that the energy separation between these two doublets, which is denoted by $k\Theta$, is greater than the exchange energy. (In (9.3) the exchange energy was assumed to be much greater than the anisotropy energy.) In the high temperature region ($T \gg \Theta$) these two doublets contribute with equal weight to the susceptibility, so that it follows from $\chi_c > \chi_a$ that A_c is larger than $\frac{1}{2}(A_\xi + A_\eta)$. In the low temperature region ($T \ll \Theta$) the lower doublet contributes the main part of the susceptibility, and, according to Nakamura and Taketa, the effective exchange interaction in this lower doublet is anisotropic and has a form $2J_a S_{1\xi}' S_{2\xi}' + 2J_a S_{1\eta}' S_{2\eta}' + 2J_c S_{1c}' S_{2c}'$, where \mathbf{S}_1' and \mathbf{S}_2' are the effective spins of magnitude one half. This anisotropic exchange interaction makes χ_c less than χ_a in the temperature range $T_N < T \ll \Theta$ because J_a is smaller than J_c —a tendency encouraged by the anisotropy of the effective g -value in this doublet. Below the Néel temperature, this anisotropic exchange interaction causes an antiferromagnetic alignment along the c -axis, so that $\chi_c - \chi_a$ remains negative. Furthermore, the theory gives a non-vanishing parallel susceptibility even at absolute zero on account of the existence of the higher doublet; this result agrees qualitatively with the experiments of Stout and Matarrese.

We have frequently emphasized the necessity of calculating the crystalline field in antiferromagnetic crystals, in order to obtain an ultimate theoretical conclusion about the anisotropy energy. Numerical calculations of this sort for FeF_2 and CoF_2 are in progress at Osaka University, and we hope that the results will be published before long.

PART III. STATISTICAL THEORY OF ANTIFERROMAGNETISM

§ 12. GENERAL REMARKS

Like ferromagnetism, antiferromagnetism is a typical example of a 'cooperative phenomenon' and has therefore been one of the favourite subjects of statistical-mechanical theories. Unfortunately, however, difficulties in the way of a rigorous treatment are even greater for antiferromagnetism than for ferromagnetism, so that none of the existent theories is satisfactory. A statistical theory usually starts from a certain molecular model without inquiring much into its deeper justification. Thus, it is customary, in the statistical treatments of antiferromagnetism, to assume the Heisenberg model (see § 4), in which the spins are coupled with each other by exchange interactions expressible by the Dirac 'vector model' formula. That is, the Hamiltonian of the antiferromagnetic system is assumed to be of the form

$$\mathcal{H}_{\text{ex}} = \sum_{jl} 2J_{jl} \mathbf{S}_j \cdot \mathbf{S}_l \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.1)$$

where \mathbf{S}_j and \mathbf{S}_l are the vector spin operators associated with the j th and l th constituent atoms of the crystal. (The sign of J_{jl} is opposite to that used in Parts I and II.) In addition to this exchange interaction, we need sometimes to take account of other kinds of energy, for instance anisotropy energy and dipolar interactions.

Although it is not certain if this formula correctly represents the molecular interactions in any real physical system, such a model is physically plausible and seems to have the properties characteristic of antiferromagnetism, so that it is the general hope that the statistical theory of this model will explain the observed behaviour of antiferromagnetic substances, at least in a semi-quantitative way. This approach is essentially phenomenological, since the interaction constant J is taken to be more or less arbitrary, and may be chosen to explain the behaviour of a given real system.

In the past ten years, great progress has been made in the general theory of cooperative phenomena. Most remarkable was the success of the rigorous theory of the two-dimensional Ising model (see the recent review of Newell and Montroll, 1953). But the theory has not been very successful for three-dimensional systems, particularly for those which require quantum-mechanical treatment rather than classical or semi-classical treatments. The fact that the spins in the Heisenberg model are quantum mechanical operators necessarily introduces great difficulties in the mathematical manipulations, which prevent us from any rigorous treatment. Thus, the quantum-statistical theory of the Heisenberg model, whether ferromagnetic or antiferromagnetic, lags far behind the classical statistical theory of cooperative systems. Of course, we may apply to our

problem the various approximation methods used for classical systems, but the criteria for their validity usually become much more obscure. It is still impossible, for instance to give any reliable estimate of the critical temperature in terms of the exchange constant.

In the statistical theory of antiferromagnetism there is another difficulty, which concerns the introduction of the long-range order parameter. Both from a theoretical and an experimental point of view, the most natural definition of this would be the partial magnetization of the crystal. Let us take the simplest case, where the whole crystal is divided into two interpenetrating sublattices, of which the magnetizations are M^+ and M^- . These are the statistical expectation values of the dynamical quantities,

$$M_{\text{op}}^+ = \mu_0 \sum_j \mathbf{S}_{jz}, \quad M_{\text{op}}^- = -\mu_0 \sum_l \mathbf{S}_{lz} \quad . \quad . \quad . \quad (12.2)$$

where j and l refer to atoms on the two different sublattices, and $\mu_0 \mathbf{S}$ ($\mu_0 = g\mu_B$) means the magnetic moment vector associated with the spin \mathbf{S} . Generally speaking, there would be no confusion in defining the order parameter if the corresponding dynamical quantity were a constant of the motion. We could then pick out those eigenstates which belong to a given value of the order parameter and construct the partition function in this subspace. This is the case for the idealized Heisenberg model of a ferromagnet, where the order parameter is the total magnetization, and the corresponding operator commutes with the exchange Hamiltonian.

On the other hand, the partial magnetizations are not constants of the motion of the spins. That is, in each of the eigenstates of the antiferromagnetic system, the partial magnetizations must have broadened distributions. In the course of the natural motion of the system, the antiferromagnetic pattern can never be conserved. Thus, it is impossible to set up a statistical distribution of the system among the eigenstates to represent an ensemble with sharply defined values of the order parameters M^+ and M^- .

It is, however, possible to calculate the probability distribution of the order parameters even if they are not constants of the motion (Kubo 1952). The probability density function for M^+ and M^- is given by

$$P(M^+, M^-) = \frac{1}{(2\pi i)^2} \iint \frac{\text{Tr} \{ \exp(-\beta \mathcal{H}) \exp(\lambda^+ M_{\text{op}}^+ + \lambda^- M_{\text{op}}^-) \}}{\text{Tr} \exp(-\beta \mathcal{H})} \\ \times \exp(-\lambda^+ M^+ - \lambda^- M^-) d\lambda^+ d\lambda^- \quad . \quad . \quad . \quad (12.3)$$

where the integral means the inverse of the Laplace integral, and λ^+ and λ^- are selector variables similar to those used in the well-known Fowler-Darwin formulation of statistical mechanics. Thus, the usual definition of the partition function may be generalized to

$$Z(M^+, M^-) = \text{Tr} \rho(M^+, M^-) = P(M^+, M^-) \text{Tr} \exp(-\beta \mathcal{H}). \quad (12.4)$$

Naturally we have

$$Z(\beta) = \text{Tr} \exp(-\beta \mathcal{H}) = \iint Z(M^+, M^-) dM^+ dM^-. \quad . \quad (12.5)$$

The partition function $Z(M^+, M^-)$ represents the relative probability of the realization of given values of the partial magnetizations. In contrast to the case where the order parameters are constants of the motion the order parameters here will assume various values, not only because of the thermal agitation, as expressed by the canonical distribution, but also because of the natural motion. Except for this complication, there is now no difference between constant and non-constant order parameters. If the partial magnetizations are really adequate to describe the physical situation, we may suppose that any radical change of the ordering pattern, for instance the reversal of all the spins, will seldom be caused by the natural motion, and therefore will have hardly any important effect on the thermodynamic behaviour of the antiferromagnet. Thus, we may assume the free energy of the system to be

$$F(M^+, M^-) = -kT \log Z(M^+, M^-) \quad . \quad . \quad (12.6)$$

which is a function of the order parameters.

We may also define a generalized partition function,

$$\mathcal{E}(\lambda^+, \lambda^-) = \text{Tr} \{ \exp(-\beta \mathcal{H}) \exp(\lambda^+ M_{\text{op}}^+ + \lambda^- M_{\text{op}}^-) \}. \quad . \quad . \quad (12.7)$$

Then we can see at once from eqns. (12.3), (12.4) and (12.6) that

$$F(M^+, M^-) = -kT \log \mathcal{E}(\lambda^+, \lambda^-) + kT(\lambda^+ M^+ + \lambda^- M^-) \quad . \quad . \quad (12.8)$$

and

$$\frac{\partial \log \mathcal{E}}{\partial \lambda^+} = M^+, \quad \frac{\partial \log \mathcal{E}}{\partial \lambda^-} = M^-, \quad . \quad . \quad . \quad (12.9)$$

provided that the integral (12.3) is reasonably approximated by means of the method of steepest descents. The transformations, (12.6), (12.8) and (12.9), are exactly those well known for the Helmholtz and the Gibbs free energies, $\lambda^+ kT$ and $\lambda^- kT$ being the intensity variables corresponding to the hypothetical magnetic fields H^+ and H^- acting on each of the sublattices. It should be remembered that H^+ and H^- are *hypothetical*, because, if they were real, we should have included them in the Hamiltonian, so that the partition function would have been

$$\text{Tr} \exp \{ -\beta (\mathcal{H} - H^+ M_{\text{op}}^+ - H^- M_{\text{op}}^-) \}$$

rather than \mathcal{E} , eqn. (12.7).

12.1. The Ising Model

The complications of the quantum-mechanical theory of antiferromagnetism are avoided if one decides to adopt the Ising model rather than the Heisenberg model. It is true that the Ising model, as a physical system, is far less satisfactory than the Heisenberg model, because it fails to describe many of the interesting features of antiferromagnetism. The Ising model may, however, be considered as an extreme case of the Heisenberg model, where an additional field is introduced, that is, an infinitely strong anisotropic field with uniaxial symmetry. This

simplification has certain advantages, in that we may use more straightforward mathematics to clarify certain statistical features of the system.

It is important to note the symmetry between ferro- and antiferromagnetic Ising models. If the lattice is divided into two sublattices and if the antiferromagnetic coupling exists only between points on different sublattices, the statistical properties of the antiferromagnet are the same as those of the ferromagnet with the same structure. This is seen at once by reversing the signs of the Ising spin variables on one of the sublattices, when the Ising spin Hamiltonian remains invariant if the sign of the exchange constant is also reversed. If the lattice structure is such that it involves closed circuits on the lattice with odd numbers of interacting bonds, then this invariant transformation is not allowed and the symmetry relation no longer holds. The triangular and hexagonal nets and the face-centred cubic structure are of this type, so that simple antiferromagnetic ordering, due to nearest neighbour interactions only, is impossible in them. The symmetry relation means symmetry of the energy level spectrum with respect to the sign of the energy. This will never be true for the Heisenberg model. The eigenvalue spectrum of the exchange Hamiltonian, eqn. (12.1), will generally be asymmetric, which means that the thermodynamic functions of the ferromagnetic and antiferromagnetic models are not related in any simple way.

Another way of looking at the Ising model is to notice that its energy expression is just the diagonal element of the Heisenberg Hamiltonian, with each spin equal to one half, in the representation diagonalizing the z -components of the spins. By the general theorem due to Peierls (1938), the free energy for the Ising model must always be higher than that for the corresponding Heisenberg model. At high temperatures, the free energies of the Ising model and the ferromagnetic and antiferromagnetic Heisenberg models approach the same asymptote. At the absolute zero, the ferromagnetic lowest energy is the same as that for a system of Ising spins but the antiferromagnetic lowest energy lies lower (see § 14). This seems to suggest that the entropy, at a given temperature, is higher for the ferromagnetic Heisenberg model, and lower for the antiferromagnetic Heisenberg model, than for the corresponding Ising model. It is unnecessary here to go into a more detailed discussion of the Ising model.

12.2. *Survey of the Approximation Methods*

The crudest approximation in the theory of cooperative phenomena is provided by the so-called molecular field theory, which is equivalent to the Bragg-Williams method, well known for alloys and regular assemblies (see, for instance, Fowler and Guggenheim 1939). When applied to antiferromagnetism, this gives the Van Vleck theory, discussed in § 4. Our general experience of cooperative phenomena suggests at once two ways of making closer approximations, which we may call the high-temperature approximation and the low-temperature approximation respectively. The moment expansion method of Heisenberg or the $1/T$

expansion method developed by Opechowski (1937, 1939) is an analogue of the Bethe–Kirkwood expansion method for a regular assembly and belongs to the first category. Another typical high-temperature approximation is provided by a quantum-mechanical version of the Bethe–Peierls method, which was first applied to ferromagnetism by P. R. Weiss (1948) and later to antiferromagnetism by Y. Y. Li (1951). The most important method for low temperatures is that of spin-waves. This was first invented by Bloch (1930) to apply to ferromagnetism and it led to the celebrated $T^{3/2}$ law for the saturation magnetization. In recent years, the application of this method to antiferromagnetism has been considerably developed.

§ 13. HIGH-TEMPERATURE APPROXIMATIONS

The most systematic approximation from the high temperature side is the $1/T$ expansion method. Let us illustrate the method for a simple model where the spin Hamiltonian is given by an exchange Hamiltonian \mathcal{H}_{ex} and the order parameters are taken to be the partial magnetizations in the z -direction.

Generally, the equilibrium values of the order parameters, M^+ and M^- , are determined by the minimum condition on $F(M^+, M^-)$ with respect to M^+ and M^- , so that the equations

$$\frac{\partial F}{\partial M^+} = \frac{\partial F}{\partial M^-} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.1)$$

give possible solutions for the ordering phenomena. By eqns. (12.8) and (12.9), eqn. (13.1) is equivalent to the conditions

$$\lambda^+ = \lambda^- = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.2)$$

Thus, we have first to solve eqn. (12.9) for λ^+ and λ^- , obtaining the expressions $\lambda^+(M^+, M^-)$ and $\lambda^-(M^+, M^-)$. Then eqn. (13.2) has solutions $M^+(T)$ and $M^-(T)$, which will be the equilibrium values if they actually give a minimum of the free energy $F(M^+, M^-)$.

Now suppose that we have found an approximation for $\log \mathcal{E}$ up to the second order terms in λ^+ and λ^- , in the form

$$\log \mathcal{E} = \frac{1}{2} (A\lambda^{+2} + 2B\lambda^+\lambda^- + A\lambda^{-2})$$

(which must be symmetrical in λ^+ and λ^- since we have assumed that the sublattices are equivalent). Then we easily find, by eqn. (12.9), that

$$M^+ + M^- = (A + B)(\lambda^+ + \lambda^-),$$

$$M^+ - M^- = (A - B)(\lambda^+ - \lambda^-).$$

Therefore, the ordinary susceptibility χ is

$$\chi = A + B,$$

whereas

$$\chi' = A - B$$

might be called the hypothetical susceptibility corresponding to the anti-parallel polarization. Spontaneous antiparallel polarization becomes

possible when χ' becomes infinitely large. In other words, the critical temperature T_c is to be determined by the condition

$$\lim_{T \rightarrow T_c + 0} 1/\chi'(T) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.3)$$

Above this temperature, $M^+ = M^- = 0$ gives the absolute minimum of the free energy $F(M^+, M^-)$.

Now, the principle of the $1/T$ expansion method is to calculate the generalized partition function \mathcal{E} , eqn. (12.7), by expanding $\exp(-\beta\mathcal{H})$ in powers of β . The calculation then reduces to the computation of the traces of various products of spin operators, which are quite elementary, though extremely tedious for higher order terms. Thus, for instance, $\chi'(\beta)$ can be calculated in the powers of β . The determination of the critical point is necessarily an extrapolation. That is, one assumes that $1/\chi'(\beta)$ can also be expanded in a power series in β , which is to be obtained from the calculated $\chi'(\beta)$. Terminating the series for $1/\chi'$ at the highest power of β to which $\chi'(\beta)$ has been calculated, one can obtain the approximation values for T_c . The first order approximation is of course that of van Vleck. The approximations up to the fourth were calculated by Kubo, Obata and Ohno (1952), whose results are listed in the table for the particular case of $S = \frac{1}{2}$. These are to be compared with the ferromagnetic

Table 3. The Antiferromagnetic Transition Points of Different Lattices
(Each atom has spin $\frac{1}{2}$.) The numerical values are those of kT_N/J .

Lattice	Number of nearest neighbours	Molecular field method	Expansion methods* (Kubo, Obata and Ohno)				Bethe-Peierls method	
			1st approx	2nd	3rd	4th	Li	Oguchi-Obata
Linear chain	2	1.00	1.00 1.243	1.00 None	None None	0.313 1.387	None	None
Quadratic layer	4	2.00	2.00 2.361	2.00 1.243	None None	0.439 2.073	None	1.582
Simple cubic	6	3.00	3.00 3.403	3.00 2.746	None None	0.654 2.710	2.004	2.618
Body-centred cubic	8	4.00	4.00 4.425	4.00 3.827	None None	0.613 3.278	3.18	3.636

* Upper figures are calculated by the expansion in $1/T$, and lower values by the expansion in terms of $x = 4 \tanh J/kT / (2 - \tanh J/kT)$.

case. The most noticeable fact is that the $1/T$ expansion gives very poorly convergent results for the antiferromagnetic case. In the ferromagnetic case, the second approximation was very bad, but it gave reasonable results in the third and fourth approximations, at least for three dimensional

lattices, as proved by the corrected calculation due to Zehler (Opechowski 1937, 1939, Zehler 1950). These are consistent with the results of P. R. Weiss (1948) based on a generalization of the Bethe–Peierls method. For the antiferromagnetic case, however, the third approximation gave no transition for any of the lattices considered, while the fourth approximation gave transition points which are considerably different from those given by Li's calculation, which will be discussed below.

In principle, the $1/T$ expansion method can also be applied to the approximate calculation of the partial magnetizations below the critical point. To do this, one calculates $\mathcal{E}(\lambda^+, \lambda^-)$ to higher order terms in λ^+ and λ^- , obtaining eqns. (13.2) as non-linear equations in M^+ and M^- . If the solution of these equations is proved to be the minimum of $F(M^+, M^-)$, this will give the equilibrium state. The underlying assumption of this method is that the free energy $F(M^+, M^-)$ is essentially analytic in β , in spite of the presence of the critical point. This assumption is necessary in order to justify the extrapolation which is involved in any of the high temperature approximations. One might object to this, pointing out that $F(M^+, M^-)$ cannot be analytic below the critical point. The problem is related to the general theory of condensation; here we only mention the fact that the high temperature approximations always involve implicitly the assumption that the whole system constitutes a single phase.

13.1. The Bethe–Peierls Method

Yin-Yuan Li applied the Bethe–Peierls–Weiss method to antiferromagnetism. The basic assumption of the method is that a cluster of $n+1$ atoms, i.e., a central atom and its neighbours, is statistically represented by the statistical operator,

$$\rho_{\text{cluster}} = \exp \left\{ (-2J \sum_{j=1}^n \mathbf{S}_0 \mathbf{S}_j - \mu_0 S_{0z} H_0 - H_f \mu_0 \sum_{j=1}^n S_{jz}) / kT \right\} \quad (13.4)$$

where H_0 is an external field and H_f the internal field representing the effect of outer atoms, which is to be determined in a self-consistent manner. Taking two kinds of cluster, one being centred on an atom of the sublattice a , and the other on the sublattice b , and assuming different internal fields H_a and H_b in place of H_f , the statistical average value of the spin on a given type of atom is calculated in two ways. Equating these expressions, one obtains two equations to be solved for H_a and H_b . For vanishing external field, one of the possible solutions is identically zero, which corresponds to the disordered state, but another non-trivial solution appears below the critical point. The values of the transition points calculated by Li are also listed in table 3, and they seem quite reasonable. In particular, Li succeeded in showing that the one- and two-dimensional lattices will not be ordered. For simple cubic and body-centred structures, the critical temperatures are somewhat higher than those for the corresponding ferromagnetic lattices. This may possibly be connected with the larger entropy of the ferromagnetic system.

13.2. *Other Approximations at High Temperatures*

Several modifications of the two standard methods discussed above have been tried by several investigators. Kubo, Obata and Ohno (1951, 1952) tried an expansion method using the parameter

$$x = 4 \tanh J/kT \{2 - \tanh J/kT\}$$

instead of J/kT . This is analogous to the expansion in power series of $\tanh J/kT$ which is known to converge well for the Ising spins. Although this expansion is good for ferromagnetism, it failed to improve the convergence of the series for the antiferromagnetic case. Oguchi and Obata (1952) proposed a modification of the Bethe–Peierls–Weiss method taking the statistical operator

$$\rho_{\text{cluster}} = \exp \left(-2J \sum_{j=1}^n \mathbf{S}_0 \mathbf{S}_j / kT \right) \exp \left(H_f \sum_{j=1}^n \mu_0 S_{jz} / kT \right) \dots \quad (13.5)$$

instead of (13.4). There is no obvious reason for preferring one of these alternatives to the other. In the formulation of Weiss and Li, H_f was interpreted as a local field, whereas in (13.5) it is a sort of selector variable similar to λ^+ and λ^- in eqn. (12.7). After reducing the complete density matrix of the whole system, we shall not get either formula exactly. Thus, one may, if one likes, use (13.5) which has the advantage that the calculation can be carried out without using any perturbation calculation, which was necessary in the former formulation. Oguchi and Obata obtained somewhat higher critical points than those given by Li. But the failure of the method for ferromagnetism makes one uneasy.

Nakamura (1953) examined another modification of the Bethe–Peierls method. He introduced some simplifications and reduced the problem to that of clusters with two spins. The results were nearly the same as those of Li's calculation. He was particularly interested in the temperature dependence of the perpendicular susceptibility below the transition point. Unfortunately, there is evidence that this, and similar calculations, are unreliable at low temperatures. Even in ferromagnetism, it has been shown that the Bethe–Weiss method leads to an anti-Curie point (Anderson 1950 c); quite 'unphysical' behaviour is also predicted for the antiferromagnetic Ising model, if the Bethe model is used (Ziman 1951). The reason seems to be that the model is quite unadapted to long range ordering, since it takes no account of the topology of the lattice, and really only treats a dozen or so spins coupled by the fictitious internal fields. The appearance of a new solution to the equations as the temperature is lowered is no argument that a new phase must occur there, and any method of checking, say, the stability of the new phase, must inevitably lead to consideration of a much more complicated model of the lattice as a whole. It does seem, however, that one may have reasonable confidence in the method when it treats short range order, where only a few spins are interacting. Li showed that the ordinary susceptibility calculated by his method is consistent with that given by the $1/T$

expansion (we cannot check the singularity because this occurs in $\chi'(\beta)$ not in $\chi(\beta)$) and it is plausible to extrapolate this curve right down to whatever transition point one might discover by other means. It is worth noting that Li's value at T_c is only 0.871 χ_{II} where χ_{II} is the constant value of the perpendicular susceptibility at low temperatures. The temperature should thus fall further, and rise further before a transition is really possible, if the perpendicular susceptibility is nearly constant in the ordered state.

Nevertheless, the theoretical situation is quite unsatisfactory and a statistical treatment giving a reliable description of antiferromagnetism around the transition point would be very welcome. Thus, there are some interesting experimental facts for which the short range order (about which the molecular field theory can tell us nothing) plays an essential role. For instance, the entropy increase in antiferromagnets above the transition point is often found to be considerable fraction of the total entropy increase. It is not clear at present how much of the residual entropy is theoretically expected at the transition point, although it seems that the statistical theory would predict a rather small amount, not more than 10% of the residual entropy, if the structure and the interaction are simple. The large residual entropy is possibly to be connected with the complicated structure of the antiferromagnetic ordering which is found to be present in many antiferromagnetic substances. For instance, Stout suggested that in an MnF_2 crystal the coupling of spins among one-dimensional arrays in the direction of the c -axis is much stronger than that between neighbouring arrays. This means that the antiferromagnetic ordering is essentially created by the weaker coupling and that the stronger coupling makes the short range order persist in each of the one-dimensional chains at high temperatures above the Néel point. A simple calculation shows that this model gives a reasonable explanation of the residual entropy, though it leaves a doubt about the absolute magnitude of the susceptibility which is also much influenced by the short range order (Stout and Kubo, unpublished). The same model was applied by Oguchi to the case of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ crystal (Oguchi, unpublished).

§ 14. LOW-TEMPERATURE APPROXIMATION AND THE ANTIFERROMAGNETIC GROUND STATES

At high temperatures, the important quantum states are those which belong to the group of levels contributing the largest amount of entropy, which means that these quantum states can be regarded, in a sense, as being highly degenerate. This allows us to treat the constituent units as nearly independent. The molecular field theories, both the crudest and the most refined, are methods of extrapolation from the high temperature regions, where they are primarily justified, to lower temperatures. On the other hand, the statistical properties at low temperatures are, of course, determined by the quantum states at the bottom of the energy

spectrum, so that the low-temperature theory always requires more detailed analysis of the quantum states of the whole system. Thus we meet here essentially a many-body problem, which can be treated usually only when some way has been found of reducing the problem to a separable system. One of the best examples of a successful low-temperature theory is the spin-wave theory of Bloch (1930) for ferromagnetism.

Since antiferromagnetism is just the opposite of ferromagnetism, the signs of the exchange integrals being reversed, and since this type of interaction is actually more common than the ferromagnetic interaction, the quantum-mechanical treatment of an antiferromagnetic system was taken up as early as 1930 by Slater. In 1931, Bethe gave a detailed mathematical theory of the spin-wave in a linear chain, in which he succeeded in treating states involving any number of reversed spins. This general theory gave, essentially, a rigorous solution for the ground state of an antiferromagnetic one-dimensional array. Some errors in Bethe's calculation were later corrected by Hulthén (1938), who solved the problem explicitly and gave an exact value for the energy of the antiferromagnetic ground state. Hulthén (1936) was also the first to apply to antiferromagnetism the semi-classical method of spin-waves due to Kramers and Heller (1934). It was, however, not until recent years that the importance of these investigations and the usefulness of the spin-wave method for antiferromagnetism became fully recognized. In 1952, Anderson re-examined the Kramers-Heller-Hulthén theory and showed that the spin-wave method can be used to give a reasonable approximation to the ground state of an antiferromagnetic array. Since then, several investigators have applied the method to the thermodynamic and dynamic properties (such as micro-wave resonance) of antiferromagnetic substances. Although the theory is still not very satisfactory, the spin-wave method is, at present, the only reasonable treatment feasible for low temperatures.

14.1. *The Bethe-Hulthén Theory for the Antiferromagnetic Linear Array*

Before going into the approximate theory of spin-waves, we shall briefly describe here the Bethe-Hulthén theory of an antiferromagnetic linear array, which is the only case ever treated in a rigorous way. Let us take the Hamiltonian

$$\mathcal{H}_{\text{ex}} = 2J \sum_j \mathbf{S}_j \mathbf{S}_{j+1}$$

and assume the spins to be of magnitude one half. The eigenfunctions of \mathcal{H}_{ex} can be expanded in the form

$$\Psi = \sum a_{n_1 n_2 \dots n_r} \Psi_{n_1 n_2 \dots n_r} \quad \dots \quad (14.1)$$

where $\Psi_{n_1 n_2 \dots n_r}$ represents the spin function of N atoms, of which r , that is, the atoms $n_1 < n_2 < \dots < n_r$, have plus spins, the rest of the atoms being orientated in the minus direction. Then, the secular equation for \mathcal{H}_{ex} can be written

$$2\epsilon a_{n_1 n_2 \dots n_r} = \sum_{n'_1 n'_2 \dots n'_r} (a_{n_1 n_2 \dots n_r} - a_{n'_1 n'_2 \dots n'_r}) \quad \dots \quad (14.2)$$

where 2ϵ is an eigenvalue of

$$-\mathcal{H}'_{\text{ex}}/J = (\mathcal{H}_{\text{ex}} - \frac{1}{2}NJ)/J \\ = -2 \sum_j (\mathbf{S}_j \mathbf{S}_{j+1} - \frac{1}{4}) \quad . \quad . \quad . \quad (14.3)$$

and the summation on the right-hand side is over all sets n'_1, n'_2, \dots, n'_r which arise from n_1, n_2, \dots, n_r by interchanging two neighbouring atoms with unequal spins. If the set n_1, n_2, \dots, n_r does not involve any neighbouring pair, eqn. (14.2) takes the form

$$2\epsilon a_{n_1 n_2 \dots n_r} \\ = \sum_j \{2a_{n_1 \dots n_j \dots n_r} - a_{n_1 \dots n_{j+1} \dots n_r} - a_{n_1 \dots n_{j-1} \dots n_r}\} \\ . \quad . \quad . \quad . \quad (14.4)$$

which at once suggests a particular solution of the type,

$$\exp [i (k_1 n_1 + k_2 n_2 + \dots + k_r n_r)].$$

Therefore the general solution can be assumed to be

$$a_{n_1 n_2 \dots n_r} = \sum_P \exp (i \sum k_{Pj} n_j + \frac{1}{2} \sum_{j < l} \phi_{Pj} p_l), \quad . \quad . \quad . \quad (14.5)$$

namely a linear combination of those functions obtained by permutation of k_1, k_2, \dots, k_r . In eqn. (14.5) \sum_P means a summation over all $r!$, different permutations of k_1, \dots, k_r , and Pj is the number which is carried to the j th place by P . In order to conserve the formal eqn. (14.4) for those cases where some of n_1, \dots, n_r are neighbours, we impose conditions such as

$$2a_{n_1 \dots n_x n_{x+1} \dots n_r} - a_{n_1 \dots n_x n_x \dots n_r} - a_{n_1 \dots n_{x+1} n_{x+1} \dots n_r} = 0. \quad (14.6)$$

The phases ϕ_{jl} in the expression (14.5) are determined by these conditions. In addition, the condition

$$a_{n_1 n_2 \dots n_r} = a_{n_2 \dots n_r, n_1+N} \quad . \quad . \quad . \quad (14.7)$$

is imposed if the chain is assumed to be a ring. Then, the eigenvalue is given by

$$\epsilon = \sum_{j=1}^r (1 - \cos k_j)$$

with the wave numbers determined by the conditions (14.6) and (14.7). Bethe and Hulthén showed that the ground state of the antiferromagnet is described by the presence of $r=N/2$ (N even) spin waves, the wave numbers being real. Other possible solutions, including those which were called the 'spin complex' states by Bethe, belong to the higher states. When the number of the atoms N is very large, eqns. (14.6) and (14.7) can be written

$$k(x) = 2\pi x + \frac{1}{2} \int_0^1 \phi(x, y) dy$$

and

$$\cot \frac{1}{2} \phi(x, y) = \frac{1}{2} \{ \cot \frac{1}{2} k(x) - \cot \frac{1}{2} k(y) \}.$$

The eigenvalue 2ϵ is given by

$$2\epsilon = N \int_0^1 (1 - \cos k(x)) dx.$$

These equations were solved exactly by Hulthén, who obtained the remarkably simple result

$$2\epsilon = 2N \log 2.$$

Thus, the lowest eigenvalue of \mathcal{H}_{ex} is

$$\begin{aligned} (\mathcal{H}_{\text{ex}})_{\min} &= -2NJ \log 2 + \frac{1}{2}NJ \\ &= -0.8863 NJ = -\frac{1}{2}NJ \times 1.7726. \quad \dots \quad (14.8) \end{aligned}$$

Note that the rigorous value is 1.7726 times lower than $-2NJ(\frac{1}{2})^2$, which is the expectation value of the Hamiltonian when the spins are aligned in an antiferromagnetic pattern in the sense of the Ising model.

14.2. Upper and Lower Bounds for the Ground Level

The lowest energy of an antiferromagnetic array is always lower than the lowest energy of the corresponding Ising model, which is the lowest of the diagonal elements of \mathcal{H}_{ex} in the representation diagonalizing the z -components of the spins. Thus we know that

$$(\mathcal{H}_{\text{ex}})_{\min} < -\frac{1}{2}Nz \times 2JS^2. \quad \dots \quad (14.9)$$

Here z is the number of the interacting neighbours, and S is the magnitude of the spins. We have assumed that the spins are all equivalent and that the lattice is divided into two sublattices. Anderson (1951) also pointed out that

$$(\mathcal{H}_{\text{ex}})_{\min} > -\frac{1}{2}Nz \ 2JS^2 \left(1 + \frac{1}{zS}\right) \quad \dots \quad (14.10)$$

gives a lower bound. This is easily seen from the fact that \mathcal{H}_{ex} can be divided into

$$\mathcal{H}_{\text{ex}} = \sum_j (2J \mathbf{S}_j \cdot \sum_l \mathbf{S}_l)$$

and that the lowest eigenvalue of each of the summands, $2J \mathbf{S}_j \cdot \sum_l \mathbf{S}_l$, is $-2JS(zS+1)$. From the variation principle (14.10) follows. If we write the lowest energy as

$$(\mathcal{H}_{\text{ex}})_{\min} = -\frac{1}{2}Nz \ 2JS^2 \left(1 + \frac{\gamma}{zS}\right), \quad \dots \quad (14.11)$$

then γ must lie between the limits

$$0 < \gamma < 1.$$

The rigorous value of γ for the linear chain is 0.7726.

14.3. Other Treatments of the Antiferromagnetic Chain

The spin functions $\Psi_{n_1 n_2 \dots n_r}$ in eqn. (14.1) may be classified according to the numbers of plus and minus spins and the number of antiparallel pairs in the chain. If one assumes a constant coefficient for the spin functions belonging to each group specified by these numbers, the eigenvalue problem of \mathcal{H}_{ex} is greatly simplified. This method was first introduced by Slater (1930), and was refined later by Hulthén (1938), who called this the 'statistical method'. Hulthén showed that the approximation is fairly good, obtaining $\gamma = 0.632$ in a first approximation

and $\gamma=0.698$ in the second approximation. He also made use of this method to calculate the (perpendicular) susceptibility, which turned out to be

$$\chi_0=0.473N\mu_B^2/2J=0.473 N\mu_0^2/8J. \quad . \quad . \quad . \quad (14.12)$$

More recently, however, Ledinegg and Urban (1953) obtained

$$\chi_0=(N\mu_B/H) \exp \{-(2cJ/\mu_B H)^{\frac{1}{2}}\}$$

by solving Hulthén's integral equation for values of energy close to the lowest level. Here c is a constant.

An interesting application of the Slater-Hulthén method was tried by Kasteleijn (1952). By a variation calculation, he treated the ground state of a linear chain with anisotropic coupling. He showed that, at the absolute zero, the antiferromagnetic ordering becomes possible only when the anisotropy exceeds a certain value. This is to be expected, since the Ising model is ordered at the absolute zero.

Syozi (1951) examined another method, which consists in writing the Hamiltonian in terms of anti-commuting operators, which, after Fourier transformation, represent the wave motion of spins. This is similar to the spinor method used for the treatment of two-dimensional Ising models (see, for instance, Kaufman 1949, Nambu 1950). The value of γ obtained by Syozi is 0.476, which indicates that the approximation is not very good.

§ 15. THE SEMI-CLASSICAL THEORY OF THE SPIN-WAVE IN ANTIFERROMAGNETIC LATTICES

If the spins are coupled by exchange forces, eqn. (12.1), the equation of motion for the spin angular momentum is given by

$$\hbar \dot{\mathbf{S}}_j = \frac{1}{i} [\mathbf{S}_j, \mathcal{H}_{\text{ex}}] = -\mathbf{S}_j \times \sum_l 2J_{jl} \mathbf{S}_l \quad . \quad . \quad . \quad (15.1)$$

the right-hand side being the torque acting on the j th spin, from the other spins, through the exchange forces. Thus, the motion of the spin system is determined by a set of non-linear equations, which hold both classically and quantum-mechanically. If there exists a stable equilibrium configuration where the torques all vanish, then by linearizing the equations we may treat the small oscillations around equilibrium, which presumably represent the low energy dynamical states of the system. This is the general principle of the spin-wave method, stated in semi-classical terms.

We shall illustrate this with some simple examples. Let us take the two-sublattice model of antiferromagnetism and assume only nearest neighbour interaction. These assumptions are easily removed or generalized, if necessary. The torques on the spins are zero for the antiferromagnetic ordering, that is, for $\mathbf{S}_j=\mathbf{S}_a$ on the sublattice a and $\mathbf{S}_l=\mathbf{S}_b$ on the sublattice b . (Of course, $\mathbf{S}_a+\mathbf{S}_b=0$ holds for antiferromagnetism in the absence of external fields, but this is not necessary for the following treatment. In fact, we shall also consider the ferrimagnetic case.)

Inserting the expressions

$$\mathbf{S}_j = \mathbf{S}_a + \delta \mathbf{S}_j, \quad \mathbf{S}_l = \mathbf{S}_b + \delta \mathbf{S}_l$$

into eqn. (15.1) and retaining only the first order terms, we get

$$\left. \begin{aligned} \hbar \dot{\delta \mathbf{S}}_j &= -\sum_l 2J_{jl} (\delta \mathbf{S}_j \times \mathbf{S}_b + \mathbf{S}_a \times \delta \mathbf{S}_l), \\ \hbar \dot{\delta \mathbf{S}}_l &= -\sum_j 2J_{lj} (\delta \mathbf{S}_l \times \mathbf{S}_a + \mathbf{S}_b \times \delta \mathbf{S}_j). \end{aligned} \right\} \quad (15.2)$$

This describes wave motion, so that we can put

$$\left. \begin{aligned} \mathbf{A}_K &= (2/N)^{\frac{1}{2}} \sum_j e^{iKj} \delta \mathbf{S}_j, \\ \mathbf{B}_K &= (2/N)^{\frac{1}{2}} \sum_l e^{iKl} \delta \mathbf{S}_l, \end{aligned} \right\} \quad (15.3)$$

where N is the total number of atoms and K is a wave number vector.

By (15.3), eqn. (15.2) is transformed into

$$\left. \begin{aligned} \hbar \dot{\mathbf{A}}_K &= -\sum_\rho 2J_\rho \mathbf{A}_K \times \mathbf{S}_b + \sum_\rho 2J_\rho e^{iK\rho} \mathbf{B}_K \times \mathbf{S}_a, \\ \hbar \dot{\mathbf{B}}_K &= -\sum_\rho 2J_\rho \mathbf{B}_K \times \mathbf{S}_a + \sum_\rho 2J_\rho e^{-iK\rho} \mathbf{A}_K \times \mathbf{S}_b \end{aligned} \right\} \quad (15.4)$$

with ρ representing the vectors connecting any one lattice point to its neighbours. Now let us choose the z -axis in the direction of \mathbf{S}_a and take the *spin-deviations*, $\delta \mathbf{S}_j$ and $\delta \mathbf{S}_l$ as the x - and y -components of the spin vectors. Using the variables

$$A_K^\pm = A_{Kx} \pm iA_{Ky}, \quad B_K^\pm = B_{Kx} \pm iB_{Ky}$$

we can write eqn. (15.4) as

$$\left. \begin{aligned} \dot{A}_K^+ &= i\omega_0(S_{bz}A_K^+ - \gamma_K S_{az}B_K^+), \\ \dot{B}_K^+ &= i\omega_0(S_{az}B_K^+ - \gamma_K S_{bz}A_K^+), \end{aligned} \right\} \quad (15.5a)$$

$$\left. \begin{aligned} \dot{A}_K^- &= -i\omega_0(S_{bz}A_K^- - \gamma_K S_{az}B_K^-), \\ \dot{B}_K^- &= -i\omega_0(S_{az}B_K^- - \gamma_K S_{bz}A_K^-) \end{aligned} \right\} \quad (15.5b)$$

where the abbreviations

$$\left. \begin{aligned} \omega_0 &= \sum_\rho 2J_\rho / \hbar, \\ \gamma_K &= \sum_\rho 2J_\rho e^{\pm iK\rho} / \sum_\rho 2J_\rho \end{aligned} \right\} \quad (15.6)$$

are used. Equations (15.5) are easily solved as follows.

15.1. Antiferromagnetic Case

In this case, we may put

$$S_{az} = -S_{bz} = S$$

so that the frequencies ω_K are given by

$$\omega_K = \omega_0 S(1 - \gamma_K^2)^{\frac{1}{2}} = \omega_e(1 - \gamma_K^2)^{\frac{1}{2}} \quad (15.7)$$

with ω_e defined by

$$\omega_e = \omega_0 S.$$

This is an important formula for the spin-wave theory of antiferromagnetism. Note that every normal mode is doubly degenerate. For small wave numbers, we may put

$$\gamma_K = 1 - \frac{1}{2}K \cdot \alpha \cdot K + O(K^2)$$

where

$$\alpha = \Sigma J_{\rho\rho} / \Sigma J_{\rho}$$

is a constant, being generally a tensor. Therefore the relation

$$\omega \propto |K| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15.8)$$

holds at the bottom of the frequency spectrum. This is to be compared with the dispersion law

$$\omega \propto K^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15.9)$$

of the spin-waves in ferromagnetism.

15.2. Ferrimagnetic Case

Although ferrimagnetism is not the subject of this review, it is of some interest to note the simple results of the spin-wave theory for this case. Here the magnitudes of the spins are different for different sublattices, which we assume to be S_a and S_b respectively. Thus we take

$$S_{az} = S_a, \quad S_{bz} = -S_b$$

in eqns. (15.5), which give the following frequencies :

$$\omega = \frac{1}{2} \omega_0 [\{ (S_a + S_b)^2 - 4 S_a S_b \gamma_K^2 \}^{\frac{1}{2}} \pm (S_a - S_b)]. \quad . \quad . \quad (15.10)$$

The degeneracy is removed here and the normal modes are separated into two branches. For small wave numbers, the dispersion law of the lower branch is (15.9), just as in ordinary ferromagnetism. This will lead to the $T^{3/2}$ law for the saturation magnetization for ferrimagnetism (Kaplan 1952).

15.3. Effects of Anisotropy and External Fields

The above treatment of spin-waves can be generalized in various ways. We may also take account of the second neighbour interactions, long range forces like dipolar interactions, the crystalline anisotropy and the effect of an external field. We can start from some ordered configuration, linearizing the equation of motion for small spin-deviations from this equilibrium state, and calculate the normal modes. Here we shall not go into such a general formulation, but will mention only a simplified case where the effect of the anisotropy is approximated by the anisotropy field \mathbf{H}_A acting on each of the spins as if it were an effective magnetic field in the direction of easy magnetization. This is allowable when the deviations from the easy axis are small. Then the torques, $\mu_a \delta \mathbf{S}_j \times \mathbf{H}_A^a$ and $\mu_b \delta \mathbf{S}_l \times \mathbf{H}_A^b$ are added to the right-hand side of each of eqns. (15.2). By \mathbf{H}_A^a and \mathbf{H}_A^b , we mean the effective anisotropy fields for the spins on the sublattices a and b , which we assume to be antiparallel to each other. For the antiferromagnetic ordering, we may take $\mathbf{H}_A^a = -\mathbf{H}_A^b$, and $S_a = S_b = S$. Thus, we find easily

$$\omega_K = [(\omega_A + \omega_e)^2 - \omega_e^2 \gamma_K^2]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (15.11)$$

instead of (15.7). Here $\omega_A = \mu_0 H_A / \hbar$ means the frequency corresponding to the anisotropy field H_A . This can be again generalized to the case

where a constant magnetic field H_0 is present in the z -direction to give the frequencies

$$\left. \begin{aligned} \omega'_K &= \omega_K + \omega_H, \\ \omega''_K &= \omega_K - \omega_H, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (15.12)$$

where ω_H is the Larmor frequency corresponding to H_0 . In particular, for long waves with $K \rightarrow 0$, we find

$$\omega = [\omega_A(\omega_A + 2\omega_c)]^{\frac{1}{2}} \pm \omega_H, \quad . \quad . \quad . \quad . \quad . \quad (15.13)$$

which are the resonance frequencies when the constant magnetic field is applied along the axis of easy magnetization. This is in accord with the formula derived by Kittel (see (6.15)). This classical model has been discussed by Keffer, Kaplan and Yafet (1953), who have given a kinematical description of the spin-wave motion.

§ 16. THE QUANTUM-MECHANICAL FORMULATION OF THE
SPIN-WAVE THEORY

In the preceding section, we have used the classical treatment only for the calculation of the normal frequencies. It is easy, in this way, to find the normal modes and their canonical coordinates and momenta, which make it possible to quantize the spin-wave normal modes. But we shall here go back to the original Hamiltonian and show that it is equivalent to a set of harmonic oscillators in a certain approximation. There are two ways of doing this, which are actually equivalent, one being the Kramers–Heller method and the other the Holstein–Primakoff formulation. In the first method, one observes that the commutation rule

$$[S_x, S_y] = iS_z \sim iS, \quad . \quad . \quad . \quad . \quad . \quad (16.1 \ a)$$

is, if S_z is nearly constant, approximately equivalent to the relation which would hold between S_x and S_y if they were canonically conjugate variables. Also, the expansion

$$S_z = [S(S+1) - S_x^2 - S_y^2]^{\frac{1}{2}} \sim S - \frac{S_x^2 + S_y^2 - S}{2S} \quad . \quad . \quad (16.1 \ b)$$

is valid in the same approximation (Anderson 1952).

The Holstein–Primakoff method consists in writing the spin operators in the following forms :

$$\left. \begin{aligned} S^+ &\equiv S_x + iS_y = (2S)^{\frac{1}{2}} \left(1 - \frac{n}{2S}\right)^{\frac{1}{2}} a, \\ S^- &\equiv S_x - iS_y = (2S)^{\frac{1}{2}} a^* \left(1 - \frac{n}{2S}\right)^{\frac{1}{2}}, \\ S_z &= S - n, \end{aligned} \right\} \quad . \quad . \quad . \quad (16.2)$$

where the operators a and a^* , called the creation and destruction operators of the ‘spin-deviation’, or briefly the spin-deviation operators, satisfy the commutation rule

$$a \ a^* - a^* a = 1, \quad . \quad . \quad . \quad . \quad . \quad (16.3)$$

and the spin-deviation n is defined by

$$a^* a = n. \quad . \quad . \quad . \quad . \quad . \quad (16.4)$$

The equivalence of (16.2) and (16.1) is easily seen if one approximates (16.2) by

$$S^+ \approx (2S)^{\frac{1}{2}} a \quad \text{and} \quad S^- \approx (2S)^{\frac{1}{2}} a^*.$$

The definitions (16.2) are consistent with the usual representation of spin operators as one can see by writing down the matrix elements, using the well-known expressions

$$(n+1 | a^* | n) = (n+1)^{\frac{1}{2}}, \quad (n-1 | a | n) = n^{\frac{1}{2}}.$$

However, it is to be remembered that the representations (16.2) are not quite the same as the original definition of the spin operators. The spin-deviation operators operate primarily in a space with an infinite dimension rather than in the space with the dimension $(2S+1)$ of the spin functions. This does not matter as long as one is carrying out rigorous calculations, because the operators S^+ and S^- never connect the proper subspace of dimension $(2S+1)$ with the rest of the infinite space. But this apparent infinity of the dimension of the spin-deviation operators seems to give rise to some difficulties when one makes use of certain approximations (Kubo 1952, 1953).

In the problem of antiferromagnetism, we introduce two kinds of spin-deviation, one for the sublattice a through the definition (16.2) and the other for the sublattice b by

$$\left. \begin{aligned} S^+ &= (2S)^{\frac{1}{2}} b^* \left(1 - \frac{n}{2S}\right)^{\frac{1}{2}}, \\ S^- &= (2S)^{\frac{1}{2}} \left(1 - \frac{n}{2S}\right)^{\frac{1}{2}} b, \\ S_z &= -S + n. \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (16.5)$$

Thus, defining the spin-deviation operators, a_j^* , a_j , b_i^* and b_i , for each of the spins, the Hamiltonian can be expressed in terms of these operators. For the two sublattice models with nearest neighbour interaction, we have

$$\begin{aligned} \mathcal{H} = & -NzJS + 2zJS (\sum_j n_j + \sum_l n_l) \\ & + 2JS \sum_{jl} \{f(n_j) a_j f(n_l) b_l + a_j^* f(n_j) b_l^* f(n_l)\} - 2J \sum_{jl} n_j n_l, \end{aligned} \quad (16.6)$$

where $f(n)$ means

$$f(n) = \left(1 - \frac{n}{2S}\right)^{\frac{1}{2}}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (16.7)$$

Now the spin-wave operators are defined by the Fourier components of the spin deviation operators

$$\left. \begin{aligned} a_K &= (2/N)^{\frac{1}{2}} \sum_j e^{iKj} a_j, & a_K^* &= (2/N)^{\frac{1}{2}} \sum_j e^{-iKj} a_j^*, \\ b_K &= (2/N)^{\frac{1}{2}} \sum_l e^{-iKl} b_l, & b_K^* &= (2/N)^{\frac{1}{2}} \sum_l e^{iKl} b_l^*, \end{aligned} \right\} \quad (16.8)$$

where the wave number vector K runs over $N/2$ points in the first zone of the reciprocal space of the lattice.

When these expressions are inserted into eqn. (16.6) and terms of order higher than the second power of the spin-deviation operators are omitted,

we obtain an expression representing spin-waves. With a little generalization corresponding to the case which leads to eqn. (15.12), we write down the spin-wave Hamiltonian in the following form :

$$\mathcal{H} = -NzJS^2 - NH_A\mu_0S + \hbar(\omega_e + \omega_A + \omega_H) \sum a_K^* a_K + \hbar(\omega_e + \omega_A - \omega_H) \sum b_K^* b_K + \hbar\omega_e \sum \gamma_K (a_K b_K + a_K^* b_K^*). \quad (16.9)$$

By the canonical transformation,

$$\begin{aligned} a_K &= x_K \cosh \delta_K + y_K^* \sinh \delta_K, & a_K^* &= x_K^* \cosh \delta_K + y_K \sinh \delta_K, \\ b_K &= x_K^* \sinh \delta_K + y_K \cosh \delta_K, & b_K^* &= x_K \sinh \delta_K + y_K^* \cosh \delta_K, \end{aligned}$$

with δ_K defined by

$$\tanh 2\delta_K = -\frac{\omega_e \gamma_K}{\omega_e + \omega_A},$$

the Hamiltonian (16.9) is easily diagonalized to

$$\mathcal{H} = -NzJS(S+1) - N\mu_0(S + \frac{1}{2})H_A + \sum_K \{ \hbar\omega_K' (n_K' + \frac{1}{2}) + \hbar\omega_K'' (n_K'' + \frac{1}{2}) \} \\ (n_K' = x_K^* x_K, \quad n_K'' = y_K^* y_K) \quad (16.10)$$

where the normal frequencies are exactly equal to those given by eqn. (15.12) (Ziman 1952, Nakamura 1952).

§ 17. CONSEQUENCES OF THE SPIN-WAVE THEORY

17.1. *The Approximate Ground Levels of Antiferromagnets*

Anderson made use of the spin-wave method for the calculation of the lowest energy of an antiferromagnetic array. In eqn. (16.10) the first term, $-NzJS(S+1)$, can be regarded as the energy at the perfect alignment of spins, if the magnitude of a spin at rest is taken as $\{S(S+1)\}^{\frac{1}{2}}$ instead of S . There is, of course, zero point motion of the spins, due to the uncertainty coming from the non-commutability of spin components, so that a certain zero point energy has to be added to the naively obtained lowest energy. This zero point motion is now organized into spin-waves, which give rise to

$$E_{\text{zero}} = \frac{1}{2} \sum_K (\hbar\omega_K' + \hbar\omega_K'') = \sum_K \hbar\omega_K, \quad (17.1)$$

where ω_K is given by eqn. (15.11). Table 4 shows the estimates for γ in eqn. (14.11) calculated by this method. This looks quite satisfactory. In particular, the close agreement with the rigorous value, $\gamma=0.7726$, for the

Table 4. Numerical Values of γ , eqn. (14.11), Calculated by the Spin-wave Method

Lattice	z	Simple spin-wave calculation	Correction by first order perturbation
Linear chain	2	0.726	0.066 S^{-1}
Quadratic layer	4	0.632	0.025 S^{-1}
Simple cubic	6	0.58	0.014 S^{-1}
Body-centred	8	0.58	0.010 S^{-1}

linear chain is remarkable. All the calculated values lie about midway between the limits, 0 and 1. This seems to suggest that the spin-wave method can be used as a reasonable approximation, although one might feel somewhat sceptical about its validity considering the fact that the spin-wave method here can give only an approximation even for the ground state, while it can start from an exact ground state in the case of ferromagnetism. In fact, the eigenfunction obtained by this method lacks the symmetry with regard to the reversal of the spins, which ought to be possessed by a rigorous solution (as that of the Bethe-Hulthén ground level). But, as Slater (1930) pointed out, the connection between the opposite types of ordering pattern is so indirect that the ground energy can be calculated to a good approximation by taking only those configurations around one of the ordered patterns. This means that the time required for the system to swing from one arrangement to its opposite is extremely large. Anderson (1952) estimated this to be of the order of years. Physically, this will also mean that the approximate eigenstates, rather than the rigorous states, are just what we are interested in, if the antiferromagnetic arrangement is ever observed.

17.2. *The Internal Energy, the Entropy and the Specific Heat*

At low temperatures, the spin-waves of low frequencies are excited. If the effect of the anisotropy is neglected, one can easily find the temperature dependence of thermodynamic quantities from the approximate dispersion law, eqn. (15.8), which is analogous to that for the Debye model of solids. Thus, for three-dimensional antiferromagnetic lattices, the internal energy E_T will be proportional to T^4 , the entropy to T^3 , and the specific heat to T^3 . These predictions are, of course, quite different from those of the molecular field theory. These relationships hold only for temperatures in the range

$$(2zJS\mu_0H_A)^{\frac{1}{2}} \ll kT \ll zJS. \quad (17.2)$$

For very low temperatures, the dependence is more rapid than any power of T (Kubo 1952).

17.3. *The Sublattice Magnetization*

The antiferromagnetic order is measured by the algebraic difference of the partial magnetizations, which may be shown to be

$$M^+ - M^- = \mu_0 SN \left\{ \left(1 + \frac{1}{2S} \right) - \frac{1}{NS} \sum_K \frac{\omega_e + \omega_A}{\omega_K} - \frac{1}{NS} \sum_K \frac{\omega_e + \omega_A}{\omega_K} \langle n_{K'} + n_{K''} \rangle \right\} \quad (17.3)$$

by the spin-wave method. The second term in the bracket is the decrease of the magnetizations due to the zero point motion. This over compensates the correction $1/2S$ in the first term, which corresponds to the last term in (16.1b). In the one-dimensional case, this zero point correction will diverge, if the anisotropy field H_A tends to zero. This is in agreement with the general expectation that the linear chain cannot be ordered even at the absolute zero, which is actually proved by Bethe and Hulthén's calculation

and is also guessed from Bloch's theory of ferromagnetism. In the two- and three-dimensional lattices the corrections are convergent in the limit of vanishing anisotropy. Thus the sublattice magnetizations are expressed in the form

$$M^{\pm} = \frac{1}{2}\mu_0 N(S - \alpha) \quad . \quad . \quad . \quad . \quad . \quad (17.4)$$

with $\alpha = 0.197$ for the square net, $\alpha = 0.078$ for the NaCl-type, and $\alpha = 0.075$ for the CsCl-type (Anderson 1952, Kubo 1952).

The decrease in magnetization with temperature is also found from eqn. (17.3). For three-dimensional lattices, the decrease will be proportional to T^2 in the temperature region (17.2) as one sees easily with use of (15.8). On the other hand, this temperature dependent correction diverges for two-dimensional lattices, which, therefore cannot be ordered except at the absolute zero. This is again similar to the consequence of the spin-wave theory for ferromagnetism.

17.4. The Magnetic Susceptibilities

The parallel susceptibility χ_{\parallel} can be calculated by the spin-wave method (Ziman 1952, Kubo 1952, Nakamura 1952, Tessman 1952). It is given by

$$\chi_{\parallel} = \frac{2\mu_0^2}{kT} \sum_K \frac{\exp(\hbar\omega_K/kT)}{(\exp(\hbar\omega_K/kT) - 1)^2} \quad . \quad . \quad . \quad (17.5)$$

This is divergent, in the limit of $H_A = 0$, for one- and two-dimensional cases, but is convergent for the three-dimensional lattices. Thus, in the temperature range (17.2), χ_{\parallel} is proportional to T^2 , for example,

$$\chi_{\parallel} \approx \frac{2N\mu_0^2}{3zJS} \left(\frac{kT}{2zJS} \right)^2$$

for body-centred structures. At lower temperatures the anisotropy field gives an exponential dependence, actually in the form

$$\chi_{\parallel} \propto T^{\frac{1}{2}} \exp(-A(H_A J)^{\frac{1}{2}} S/kT)$$

where A is a constant. At higher temperatures, eqn. (17.5) shows that χ_{\parallel} becomes proportional to T rather than to T^2 . But this is an extrapolation beyond the limit of the theory.

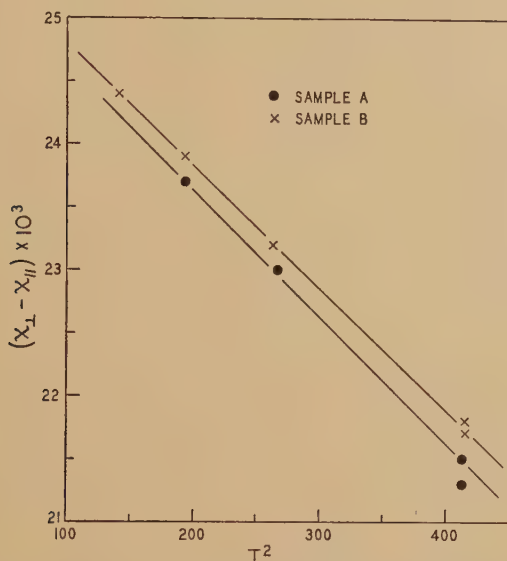
When an external field is applied in a direction perpendicular to the spontaneous magnetizations, the magnetic energy, $-\mu_0(\sum_j S_{xj} + \sum_l S_{xl})H_x$ is to be considered. In the spin-wave formulation, this energy involves only the waves of zero wave-number which means that the effect is only to displace the equilibrium point of these oscillators. Therefore, the decrease of the total energy is entirely static in this approximation, so that the perpendicular susceptibility is obviously independent of temperature. Thus we can show at once that

$$\chi_{\perp} = \frac{N\mu_0^2}{4zJ} \quad . \quad . \quad . \quad . \quad . \quad (17.6)$$

which is the same as that which follows from Néel-van Vleck theory.

Figure 28 shows the T^2 -dependence of $\chi_I - \chi_{II}$ observed by Griffel and Stout (1950). For other crystals, like FeF_2 , CoF_2 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, there is evidence that the temperature dependence is faster than T^2 (Stout and Matarrese 1953, van den Handel, Gijsman and Poulis 1952, Poulis and Hardeman 1953). This is perhaps to be attributed to the anisotropy effect.

Fig. 28



Molal magnetic anisotropy $\chi_I - \chi_{II}$ of MnF_2 . Experimental data by Griffel and Stout (1950).

§ 18. FURTHER REMARKS AND SUMMARY

18.1. Higher Approximations

The spin-wave theory so far discussed is based on the simplification that it neglects the collisions, or the interactions between spin-waves. Obviously, this is not valid if the concentration of spin-wave quanta is increased. Thus, the approximation of Bloch's theory of ferromagnetism becomes poor when the temperature is raised to about one-tenth of the Curie point, which will presumably be true also for the spin-wave theory of antiferromagnetism. Furthermore, the approximate nature of the antiferromagnetic ground state of the spin-wave method seems to indicate that the interaction between spin-waves is even more important for antiferromagnetism than for ferromagnetism.

The effect of this interaction, which is represented by the higher order terms in the spin-deviation operators, may be examined by the perturbation method. The first difficulty here is to find out what these higher order terms should be. The discrepancy between the spaces in which the spin operators and the spin-deviation operators are operating necessarily introduces a certain ambiguity in the definition of the perturbation terms.

The simplest, and perhaps most natural way, is to choose the higher order terms of the binomial expansion of $f(n)$, eqn. (16.7),

$$f(n) = 1 - n/4S + \dots \quad (18.1)$$

as the correction terms. One easily sees that this procedure corresponds to an expansion in powers of $1/S$. That is, the classical treatment of spins in the limit of $S \rightarrow \infty$ is the zeroth order approximation, the first order approximation being afforded by the spin-wave theory expressed by the Hamiltonian (16.9). In the second order approximation, one has to consider the correction terms coming from the second term of (18.1) and also from the last term of eqn. (16.6).

Kubo (1952) showed that reasonable approximations are obtained by this procedure in the second order. For instance, the corrections to the ground energies come out to be less than 10% of the preceding corrections (see table 4). The perpendicular susceptibility χ_{\perp} at the absolute zero decreases by an amount depending on the magnitudes of the spins but of the order of 10%. This is consistent with Hulthén's result for the one-dimensional case, and also with the sign of the change of χ_{\perp} with temperature predicted by Hulthén (1936) in the general case. The temperature dependence of the perpendicular susceptibility is of some interest. If the decrease is real, it means that the susceptibility at the Néel point must be smaller than that predicted by the van Vleck theory. The observed decrease of χ_{\perp} in MnF_2 might be correlated with this effect but a recent measurement by Bizette (1954) shows that it is almost independent of temperature; the strong temperature dependence of χ_{\perp} observed, for instance, in FeF_2 and CoF_2 is more likely to be attributed to the anisotropy effect (Stout and Matarrese 1953).

An alternative approach to this problem has been given by Ziman (1952, 1953). Instead of expanding the (operator) function $f(n)$ in a power series in n , and using perturbation theory, he has replaced the operator by its average expectation value, calculated in a 'spin-wave state'. The method is not justified rigorously but is, in a sense, not unlike a molecular field method, in that a factor is introduced which weakens the coupling between the spins as they become more disordered, and this factor is then calculated by a self consistency argument. The correction to the ground energies is much the same as that found by Kubo, but Ziman has concluded that χ_{\perp} should remain constant, even when the interactions have been taken into account, and he has shown (unpublished thesis) that the difference between this result and the result obtained by Hulthén is due to the neglect by the latter of the effect of disorder on the commutation properties of the (approximate) spin-wave operators.

The general effect of the interactions is to crowd the spin-wave levels closer and closer as they become more and more excited, so that χ_{\parallel} tends to rise fairly steeply above the T^2 curve. Ziman has suggested that this might give a fair approximation to the Néel temperature, defined as the point where $\chi_{\parallel} = \chi_{\perp}$. It is admittedly a crude extrapolation, but some of the results are interesting. Thus, it is found that the

Néel temperature is proportional to $JS(2S+1)$ and in all cases lies much below that calculated by the molecular field and Bethe-Weiss methods. This is not surprising, since in this method the 'zero point disorder' of the ground state is included, so that less further disorder, i.e. less temperature, is needed for the antiferromagnetism to break down entirely.

It was also possible to calculate the transition points for the body-centred and face-centred structures, taking account of the next nearest neighbour interactions. If r represents the ratio of these to the nearest neighbour interaction, then it can be shown that for the face-centred lattice, when $r \rightarrow 0.5$, the critical temperature tends to zero. This value of r corresponds to a change from one type of ordering to another, and at exactly this special value the lattice cannot decide between the two types, and remains disordered. It is concluded that the value $r=0.5$ predicted by Anderson (1950 b—see eqn. (4.22) above) for MnO , on the basis of observed values of θ/T_N , cannot be correct. The larger values of r , near to unity, are in accord with the theory of interactions, where super exchange plays an even more important role than the direct exchange. The case of the body-centred structures is similar.

18.2. *Difficulties of the Spin-Wave Method*

The perturbation calculation, however, runs into difficulties over convergence, especially when one uses any other method than the binomial expansion of $f(n)$, eqn. (18.1). For instance, if $f(n)$ is defined by $f(n)=(1-n/2S)^{\frac{1}{2}}$ for $0 \leq n \leq 2S$ and $f(n)=0$ for $n > 2S$, then the first order perturbation diverges in many cases. The perturbation to the ground state energy becomes infinite for a one-dimensional chain, although it remains small for three-dimensional lattices. The situation becomes worse if one goes to the calculation of the magnetization or the susceptibilities. For these, the perturbation will diverge even for three-dimensional lattices, in the limit of vanishing anisotropy. This is certainly very discouraging to attempts to improve the approximations of the spin-wave method along the lines of a perturbation calculation, but further investigations are needed.

This divergence in the perturbation method is closely connected with another difficulty of the spin-wave theory, which is revealed by the fact that the fluctuations in the magnetizations calculated by this method are quite anomalous (Kubo 1952). The temperature dependent parts of the fluctuation of the partial magnetizations are divergent for lattices of all dimensions in the limit of $H_A \rightarrow 0$. The same is also true for the ferromagnetic case. Closer examination shows that these fluctuations are of the order of $N^{4/D}$, D being the dimensions. If the anisotropy is taken into account, then they become normal, that is of the order of N . This abnormal fluctuation might, at first sight, be correlated with the free rotation of the spins in the absence of the anisotropy field. But this possibility is eliminated, at least for the calculation of the magnetization, by the condition that the quantum number of the spin-wave with infinitely

long wave length be zero. It seems more likely that this kind of divergence is related to the apparent infinity of the dimension of the space for the spin-deviation operators and to the inadequacy of the spin-wave method for such calculations. Perhaps it should be noticed here that the fluctuation is physically significant, because it is essentially the sum total of the short range order which is present in ordered states in excess of the long range order. Thus it should be observable, at least in principle, by neutron experiments.

The abnormal fluctuation is also inconsistent with the current picture of the spin ordering, which describes the spins as being aligned primarily by strong exchange forces, the resultant moving around in the anisotropy and external fields. This means that the anisotropy and external fields can be thought of as perturbations. The divergence of the spin-wave theory is, in fact, avoided if one always takes the anisotropy field into account. But, it then means that the importance of the anisotropy field is far greater than one has ever thought and the effect of anisotropy can never be treated separately. The calculated fluctuation of the partial magnetizations is finite at the absolute zero, because of the zero point motion. The temperature dependent part is proportional to the inverse square root of the anisotropy constant, if a finite anisotropy is assumed. But we cannot be confident of this, for the reasons we have just discussed. On the other hand, it must be admitted that the actual amount of anisotropy energy required to reduce the fluctuations to normal is very small, so that for many purposes it does not appear explicitly in the final formulae, but has only been used as a 'convergence factor', which has cancelled out during the calculation. It is inconceivable that a real physical antiferromagnetic array should not have *some* anisotropy energy available to stabilize it, and the apparent divergence of certain quantities as $H_A \rightarrow 0$ may merely be a formal mathematical description of the instability of the system in that unusual case.

A possible way of avoiding the difficulty was suggested by Kubo (1953), who applied the spin-wave theory as a variational method. This method is, in principle, analogous to the Hartree-Fock method known for many-electron systems. The coupled spin-wave system is now approximated by a set of independent spin-wave oscillators which are to be chosen in a self-consistent manner to minimize the energy or the free energy of the whole system. The collisions of spin-waves result in a certain modification of the frequency spectrum, which removes the divergence difficulties in the limit $H_A=0$.

18.3. Summary

Although the simple spin-wave method has some difficulties, it has been successful in giving some physical insight into antiferromagnetism. The approximation is generally better for lattices of higher dimensions and for larger magnitudes of the spins. Thus, for the actual crystals of three-dimensional structure, it is able to give fairly reliable predictions

about the free energy, the entropy, the partial magnetizations, and the magnetic susceptibilities at low temperatures. The great advantage of this method is that it can easily be generalized. For instance, second neighbour interactions and dipolar forces can be taken into account (Ziman 1952, Tessman 1952). The quantization axes of the spins may also be chosen arbitrarily. Thus one can start by assuming some directions to be those of the antiferromagnetic ordering and construct the spin-wave Hamiltonian to represent small deviations from this order. The assumed directions can be determined by the variation principle to minimize the total energy or the free energy. This can be applied to the general consideration of anisotropy and external fields (Kubo 1953).

But the mathematical difficulties are great for such refinements of the theory as the application to higher temperatures and the calculation of higher order quantities such as the fluctuations or the short range order.

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